SYNTHESIS AND CHARACTERIZATION OF Ni BASED NANO CARBON ENERGETIC MATERIALBY ELECTRODEPOSITION TO PRODUCE CLEAN ENERGY IN ALCOHOLIC FUEL CELL

A Thesis Submitted in partial Fulfilment of
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BY
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Certificate of Approval

This is to certify that the entitled **‘*SYNTHESIS AND CHARACTERIZATION OF Ni BASED NANO CARBON ENERGETIC MATERIALBY ELECTRODEPOSITION TO PRODUCE CLEAN ENERGY IN ALCOHOLIC FUEL CELL’*** has been carried out by **Mr.Nishant kumar Singh(Examination Roll No: M4MET19001 , Registration No: 140890 of 2017-2018)** under my guidance and supervision and accepted in partial fulfilment for the degree of Master of engineering in Metallurgical Engineering from Jadavpur University. To the best of our knowledge the contents of this thesis or any part thereof have not been previously submitted for the award of any degree or diploma.

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I do here by solemnly declare that the work embodies in this thesis entitles "***SYNTHESIS AND CHARACTERIZATION OF Ni BASED NANO CARBON ENERGETIC MATERIALBY ELECTRODEPOSITION TO PRODUCE CLEAN ENERGY IN ALCOHOLIC FUEL CELL***" is the orginal investigation carried out independently by me under the supervision of Prof.S.Paul Department of Metallurgical and Material Engineering ,Jadavpur University ,Kolkata, India for the award of the degree of Maste of engineering (Metallurgical Engineering) of Jadavpur University . To based of my knowledge and belief ,this work has not been presented for any degree or distinction under any other university.

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The forging thesis is hereby approved as a credible study of an engineering subject and presented in a manner satisfactory to warrant acceptance as pre-requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve the thesis only for which it is submitted.

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Signature of examiners

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CONTENTS

ABSTRACT

Energy synthesis through alternative pollution free route is the most thrust area of research to fulfil the rising demand of energy in the developed and developing hi-tech cities. Fuel cells produce clean energy on electro-oxidation of organic fuels on electro catalytic electrodes. platinum and Platinum based alloys are used as electrode materials in fuel cells as they have excellent electro catalytic properties Development of fuel cells to meet the energy crisis from laboratory scale to industrial scale lies on the development of cheaper high energetic materials .Ni and Ni based alloys has been found to have electro catalytic properties and is being used as electrodes for batteries . Similarly Zn, Al also have catalytic activity and find their use in battery technology.

In the present investigation of the project two new electro-catalytic material Ni-NiO based nano carbon have been developed by electrodeposition on Al surface .. The variable in the electrodeposition technique were deposition current density, electrolyte chemistry and temperature

The performances of the materials were investigated by electrochemical characterisation CV (cyclic voltammetry), CA (chronoamperometry) Pd polarization) (potentiodynamic

and EIS (Electrochemical Impedance Spectroscopy). The materials were further characterised by XRD (X Ray Diffraction) to know the constituents of the coatings and SEM (Scanning Electron Microscopy) to find out the morphology of the coatings.

CHAPTER 1

INTRODUCTION

Introduction

The demand for energy is growing every day, due to fast urbanization, fulfillment of our daily needs and the progress of world economy. The energy demand has been mostly fulfilled by conventional energy resources, such as coal, natural gases, etc. However, the energy harvesting from these resources creates a lot of polluting gases, hazardous substances which have a very harmful impact on global environment, leading to health hazardous problems, not acceptable to the governments of developed and developing nations. So, the production of pollution free renewable energy at an economically viable price is a huge challenge to researchers and scientists. A fuel cell, operated with renewable fuels, is such a kind of alternative technology, to produce clean renewable energy .

In a fuel cell, fuel is electrochemically oxidized at the electro catalytic anode surface, knocking the electrons from the fuel, and transferring them in the form of current through the electrode and current collector to the external circuit. The energy conversion efficiency, by this route of thermal to mechanical energy, is not limited by the Carnot cycle heat engine, and hence, is very high. Direct Ethanol Fuel Cell (DEFC) is one of the most promising electrical energy producing units from clean renewable energy technology.

In the present paper, Nickel was electro-chemically deposited on the Al foil using direct current (DC) varying depositing potential,time, temperature and chemistry of the electrolyte. Nano Carbon was codeposited with Ni to enhance the electrocatalytic property of the material .

The presence of electro deposited nickel was confirmed by XRD, and the coating surface morphology was revealed by scanning electron microscope (SEM). Electrocatalytic activities of the developed materials towards ethanol electro oxidation were characterized by cyclic voltammetry (CV), chronoamperometry (CA), and potentiodynamic polarization tests. Electrochemical Impedance Spectroscopy (EIS) studies were also performed to compute polarization resistance, Impedance and double layer capacitance. The R-L-C circuit evaluated from EIS studies helped to understand the fundamental science of find high energetic material on ethanol oxidation by Ni and Ni- Nano- C coatings.

The investigation opens up an idea to fabricate an inexpensive fuel cell with Nickel –Nano Carbon coated electrodes to produce clean electrical energy at lower cost from ethanol and bio ethanol derived from agriculture waste.

CHAPTER 2

LITERATURE REVIEW

2. Literature Review

2.1 Fuel cell:

A fuel cell is an electrochemical "device" that converts chemical energy content of a fuel say, H_2 into electric energy by electrochemical oxidation of the fuel over a electrocatalytic anode surface, releasing electron to the external circuit. The ionized fuel (H^+) is oxidized by an oxidizer like O_2 of air .

2.1.1 Working Principle:

A fuel cell is a device that uses hydrogen (or hydrogen-rich fuel) and oxygen to create electricity by an electrochemical process.

A single fuel cell consists of an electrolyte sandwiched between two thin electrodes (a porous anode and cathode) .

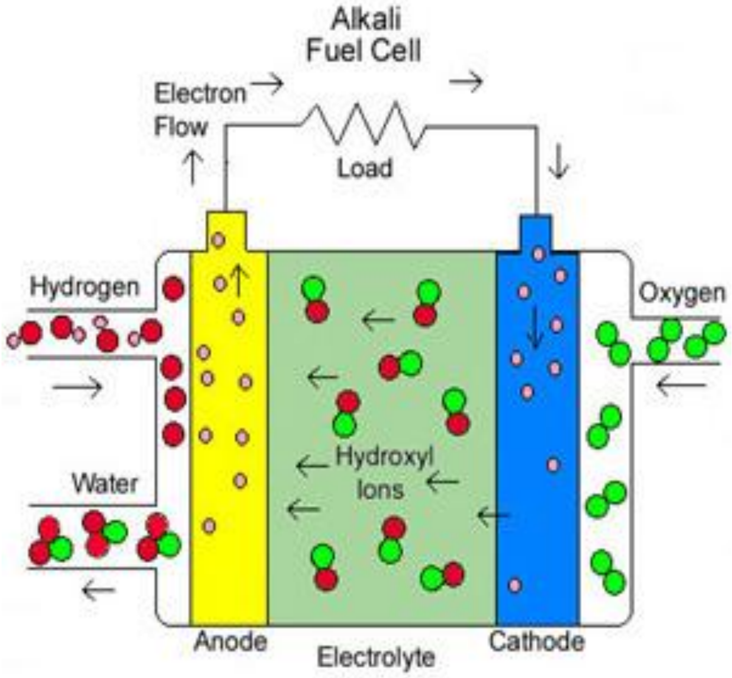


Fig 2.1 working a hydrogen fuel cell.

Hydrogen, or a hydrogen-rich fuel, is fed to the anode where a catalyst separates hydrogen's negatively charged electrons from positively charged ions (protons)

At the cathode, oxygen combines with electrons and, in some cases, with species such as protons or water, resulting in water or hydroxide ions, respectively

The electrons from the anode side of the cell cannot pass through the membrane to the positively charged cathode; they must travel around it via an electrical circuit to reach the other side of the cell. This movement of electrons is an electrical current.

The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the temperature at which it operates, and the pressure at which the gases are supplied to the cell .

Still, a single fuel cell produces enough electricity for only the smallest applications. Therefore, individual fuel cells are typically combined in series into a fuel cell stack. A typical fuel cell stack may consist of hundreds of fuel cells.

The reactions are given below.

Anode: $2H_2 \text{-->} 4H^+ + 4e^-$

Cathode: $4e^- + 4H^+ + O_2 \text{-->} 2H_2O$

Overall: $2H_2 + O_2 \text{-->} 2H_2O$

The ideal available electrical work (assuming no losses by heat) from the electrons flowing through the circuit is $W_{max} = -n F E$

Where E is the cell potential , n is the number of charged involved , F is the faraday.

n = 2 ; F = 96,493 Coulombs per equivalent, E = cell potential under reversible condition = 1.229v

1 coulomb = 0.000278 Ah , Wmax = 66 watt.hour per mole of H_2 gas.[1]

2.1.2 Types of Fuel Cell :

Fuel cells are classified primarily by the kind of electrolyte they employ. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. Most fuel cells are powered by hydrogen, which can be fed to the fuel cell system directly or can be generated within the fuel cell system by reforming hydrogen-rich fuels such as methanol, ethanol, and hydrocarbon fuels.

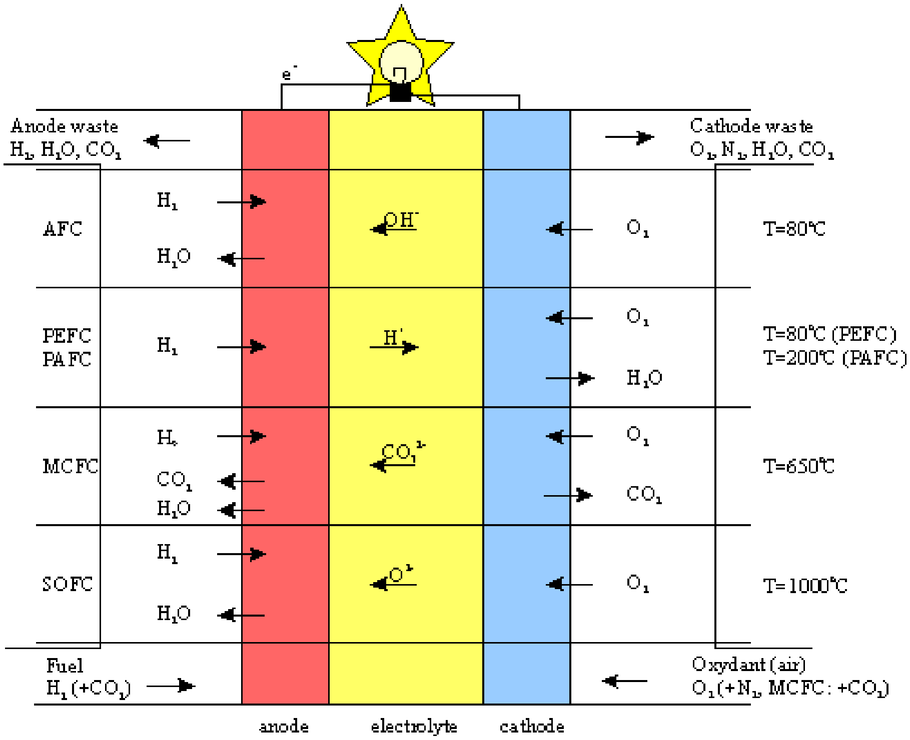


Fig 2.2 schematic diagram giving a comparison of some common type of fuel cell.

Solid Oxide Fuel Cell (SOFC) :

They operate at high temperatures (1000-1100 ° C) and a practical efficiency 50-60%. They are not the most reactive because of the low conductivity of its ionic conducting electrolyte (yttriastabilised zirconia). Because of the conductivity and heat, They have been used in large power plants which can use the cogeneration of steam for additional power. The primary drawback to this type of fuel cell is the cost of containment which requires ceramics which are difficult to fabricate in forms and shapes that can accommodate the high thermal stresses. They can be .used in power back for out door recreation (small tubular system) and in micro CHP systems in residences.

Electrochemical equation:

Anode: H2 + O2 ® H2O + 2 e-
Cathode: ½ O2 + 2e- ® O2-
Cell: H2 + ½ O2 ® H2O

The principle of operation of the SOFC is straightforward: oxygen atoms are reduced on the porous cathode surface by electrons. The resulting oxide ions diffuse through the electrolyte to the fuel-rich and porous anode, where they react with the fuel (hydrogen and/ or carbon monoxide) and give off electrons to an external circuit.

During the operation of the cell, a large amount of heat is produced by the electrochemical reaction, which does not have to be wasted: it can be utilized by an integrated heat management system. Since it takes a long time to reach its operating temperature, the best applications for SOFCs are ones that use both the heat and electricity generated, such as stationary power plants and auxiliary power supplies. Problems with start-up time could be solved by using supercapacitor batteries for the first few minutes of operation in mobile applications.

Stabilized zirconia (ZrO2 doped with Ca, Mg, or Y) was an insulator at room temperature, an ionic conductor from 600–1,000 ° C and a mixed conductor (both electronic and ionic) at around 1500 ° C. Both electrodes (cathode and anode) are made of sophisticated ceramic materials, since the high operating temperature determined by the ceramic electrolyte prevents the use of cheaper, less refractory metals.

The big advantage of the SOFC over the molten carbonate fuel cell (MCFC) is the solid nature of the electrolyte, so that there are no pumps required to circulate a hot and corrosive melt. The operating temperature is between 600 and 1,000 ° C, depending on the generation of the fuel cell (first, second, and third, with, respectively, decreasing operating temperatures). Both hydrogen and carbon monoxide serve as direct fuels, but common hydrocarbon fuels (diesel, natural gas, gasoline, alcohol, etc.) can be supplied to an SOFC.

Electrolyte: The most widely used material is yttriastabilized zirconia (YSZ); next popular electrolyte materials are doped ceria, CeO2, and doped lanthanum gallate, LaGaO3 (both are oxygen ion conductors); and doped barium zirconate, BaZrO3 (a proton conductor). The concentration and type of dopants influence the material properties strongly; ionic radius and ion charge are the principle characteristics. In an oxide ion conductor, current flows by the movement of oxide ions through the crystal lattice. This is a thermally activated process, where the ions hop from one site to another (from one potential valley to another) in a random way. When an electric field is applied, there is a drift in one direction superimposed on the random thermal motion. Ionic conduction depends on the mobility of the ions and therefore on temperature. At high temperatures (600–1,000 ° C), the conductivity can reach 100 S m − 1, which is of the same order of magnitude as for liquid electrolytes. Only a limited number of materials, such as fluorite-structure oxides, perovskites, the LaMeOx (LAMOX) and BiMeVOx (BIMEVOXes) families facilitate fast oxygen ion migration. Fluorite oxides are the most common and classical oxygen ion conducting materials.

Electrodes :The cathode material is very important because usually the oxidation reaction determines the efficiency of the fuel cell. Since cathodes operate in a highly oxidizing environment, it is impossible to use cheap base metals. The best compromise is semiconducting oxides, such as doped lanthanum cobaltites and lanthanum manganites. Nickel is used as the anode because it is economical and exhibits high performance. Ni is susceptible to become coated with a carbon layer when it reacts with carbon-based fuels. Coke formation usually impedes further reaction from happening but certain additives to the Ni + YSZ cermet, such as 5% ceria or 1% molybdena inhibit carbon deposition. Besides catalyzing the oxidation of hydrogen, Ni is also active in reforming carbon-containing fuels.

Molten Carbonate Fuel cell:

They operate at 600 ° C and can use CO as a fuel input on the cathode side but need hydrogen on the anode. The temperature is high enough to be used for additional power production through cogeneration of steam. The efficiency of these type of fuel cells has risen to 50% in a combined (electrical and steam) cycle. They can also be used in mega-watt size power plants because of their heat.

Electrochemical Equation:

Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

Cathode: $\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

Cell: $H_2 + \frac{1}{2} O_2 + CO_2 \rightarrow H_2O + CO_2$

A molten mixture of salts comprising lithium, sodium, and potassium carbonates is used as the electrolyte. These salts melt and conduct carbonate ions (CO_3^{2-}) from the anode to the cathode when heated to about 600 ° C. Hydrocarbons have to be used as part of the fuel since the charge carriers in the electrolyte –carbonate ions –have to be supplied. Hydrogen, which can be generated internally by reforming hydrocarbon-based fuels, is also needed at the anode. The electrodes should therefore be resistant to poisoning by carbon. The high exhaust temperature makes cogeneration of electricity with turbines possible; hence the efficiency –60% without and 80% with hybrid technology –is relatively high compared to other fuel cell systems. MCFCs are mainly utilized for stationary power generation in the 50 kW to 5 MW range. Since it uses a liquid high temperature electrolyte, it is rather unsuitable for mobile applications. The main problem with MCFCs is the slow dissolution of the cathode into the electrolyte. Most of the research is therefore in the area of more durable materials and cathodes.

Electrolyte : the MCFC is made of a lithium–potassium carbonate salt heated to 600–1,000 ° C. At this temperature, the salt is in the liquid phase and can conduct ions between the two electrodes. The typical mixture ratio of the electrolyte is 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 (Li/ K = 62/ 38). This particular mixture of carbonate salts melts at 550 ° C, and when it infiltrates a porous lithium aluminate ($LiAlO_2$), a ceramic matrix, it functions both as an ion-conducting electrolyte and gasketing for the fuel cell stack. Negative carbonate ions (CO_3^{2-}) are responsible for conduction.

Electrode : A significant advantage of the MCFC is that non-noble metals can be used as electrodes. At the high operating temperature, a nickel anode and a nickel oxide cathode is able to promote the electrochemical reaction. This means lower production costs compared to low temperature fuel cells, where platinum has to be added to the electrode as a catalyst. The Ni electrodes are less prone to CO poisoning, hence coal-based fuels can be used, especially since internal reforming can take place.

Proton Exchange Membrane (PEMFC):

PEM fuel cells operate at around 80 ° C and a practical efficiency of 60%. Power output is in the range of 5-200 kW. They are ideal for transportation and portable power. Additional advantages are their high response , the small size and low cost. An attractive future development is the Direct Methanol Fuel Cell (DMFC). This uses methanol as a fuel for fuel cells by reforming it into hydrogen because of the capacity of safe hydrogen storage and transportation that methanol provides. DMFC is basically used in transportation.

Electrochemical Equation:

Anode: H_2 ® $2H^+ + 2e^-$

Cathode: ½ $O_2 + 2H^+ + 2e^-$ ® H_2O

Cell: H_2 + ½ O_2 ® H_2O

The fuel cell uses a polymeric electrolyte. The proton conducting polymer forms the heart of each cell; electrodes, usually made of porous carbon with catalytic platinum incorporated into them, are bonded to either side of the electrolyte to form a one-piece membrane–electrode assembly (MEA). The following are some key advantages that make PEMs such a promising technology for the automotive market:

- Low temperature operation
- Quick start-up
- Absence of corrosive liquids

The PEMFC is constructed in layers of bipolar plates, electrodes, and membranes .Each individual cell produces about 0.7 V EMF when operating in air. In order to generate a useful voltage, the electrodes of multiple cells must be linked in series. In addition to connecting the cells, we must ensure that reactant gases can still reach the electrodes and that the resistance of the electrodes has a minimal effect. A bipolar plate is used to interconnect the anode of one cell to the cathode of the next. It must evenly distribute reactant gases over the surface of the anode, and oxygen/ air over the cathode.

Bipolar plates may also need to carry a cooling fluid and, in addition, need to keep all these gases and cooling fluids separate. Following design considerations need to be emphasized

● The electrical contacts should be as large as possible

● The plate should be thin to minimize resistance

● Gas needs to flow easily across the plate

Electrolyte: Nafion ion exchange membrane forms the basis of the PEMFC. Nafion is a polymer based on polytetrafluoroethylene, containing a fraction of pendant sulfonic acid groups (“sulfonic acid group”usually refers to the undissociated SO_3H group, whereas “sulfonate”refers to the ionized SO_3^- group after the proton has dissociated.

Electrode: In the first fuel cells, platinum was used in relatively large quantities. This led to the mistaken belief that most of the cost of a fuel cell came from the platinum content. Generally this is no longer the case. Platinum particles are deposited very finely onto carbon powders, so that the platinum is very carefully dispersed with a maximal surface area. With catalysts produced in this way, the raw material platinum cost is just US $ 10 for a 1-kW cell stack. Before the catalyst layer is applied to the electrolyte, a coating of soluble electrolyte is brushed onto it. This ensures that there is good contact between the platinum and the electrolyte to achieve the important three-phase interaction between gas, catalyst, and electrolyte necessary for the reaction to proceed.

The catalyst can be applied to the membrane in one of two ways: either directly onto the membrane in the form of a catalyst powder or alternatively by rolling, spraying, or printing, and adding the supporting electrode structure –often called the gas-diffusion layer –afterward, see Figure 4.6 b. The electrodes can also be assembled separately and bonded to the membrane in their complete form by hot pressing. The catalyst powder is sometimes mixed with PTFE to drive out product water and prevent the electrode from becoming water logged. A “gas diffusion layer”is added between the catalyst and the bipolar plate to provide some rigidity to the MEA and to ensure ease of diffusion. This layer is usually composed of carbon cloth or carbon paper 0.2–0.5-mm thick, with more PTFE added to expel water. PEM is a solid-state electrolyte that functions at around 80 ° C. Compared to the 700–1,000 ° C at which the solid oxide electrolytes become conductive, this is a low temperature.

Phosphoric Acid Fuel Cell (PAFC) :

Phosphoric Acid fuel cells (PAFC) use phosphoric acid as the electrolyte. Efficiency ranges from 40 to 80 percent, and operating temperature is between 150 to 200 degrees C (about 300 to 400 degrees F). PAFCs tolerate a carbon monoxide concentration of about 1.5 percent, which broadens the choice of fuels they can use. If gasoline is used, the sulfur must be removed. Platinum electrode-catalysts are needed, and internal parts must be able to withstand the corrosive acid.The efficiency of this system is much lower than that of the other systems at 40%. It is the FC that has mostly been exploited, mainly due to its high grade heat, which can be used in small-scale CHP especially at military sites and UPS systems fuelled with hydrogen, natural gas, LPG and methane from waste water purification plants.. The power output varies from 200 kW to 20 MW. The main disadvantage is that it has no self-starting capability, because at lower temperatures (40-50 ° C) freezing of concentrated Phosphoric Acid occurs. In order to reduce losses, the cathode catalyst and the reformer need to be improved.

Electrochemical Equation:

Anode: H_2 ® $2H^+ + 2e^-$

Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^-$ ® H_2O

Cell: $H_2 + \frac{1}{2} O_2$ ® H_2O 4.4.5

Alkaline Fuel Cell (AFC):

The fuel cells operate on compressed hydrogen and oxygen. They generally use a solution of potassium hydroxide (chemically, KOH) in water as their electrolyte. Efficiency is about 70 percent, and operating temperature is 150 to 200 degrees C, (about 300 to 400 degrees F). Cell output ranges from 300 watts (W) to 5 kilowatts (kW). Alkali cells were used in Apollo spacecraft to provide both electricity and drinking water. They require pure hydrogen fuel, however, and their platinum electrode catalysts are expensive. And like any container filled with liquid, they can leak. Their excessive cost and sensitivity to CO_2 , have restricted their research and development, no matter their high efficiency and power density.

Electrochemical Equation:

Anode: $H_2 + 2(OH)^-$ ® $2H_2O + 2e^-$

Cathode: $\frac{1}{2} O_2 + HO_2 + 2e^-$ ® $2(OH)^-$

Cell: $H_2 + \frac{1}{2} O_2 + CO_2$ ® H_2O

Direct Methanol Fuel Cell (DMFC):

Most fuel cells are powered by hydrogen, which can be fed to the fuel cell system directly or can be generated within the fuel cell system by reforming hydrogen-rich fuels such as methanol, ethanol, and hydrocarbon fuels. Direct methanol fuel cells (DMFCs), however, are powered by pure methanol, which is mixed with water and fed directly to the fuel cell anode. The operating temperature is 60 -100 C.

Anode Reaction : $CH_3OH(l) + H_2O(l) .= CO_2(g) + 6H^+ + 6e^-$, $Ea = -0.016V$ (1)

Cathode Reaction : $1.5O_2(g) + 6H^+ + 6e^- = 3H_2O(l)$, $Ec = 1.229V$ (2)

Overall Reaction : $CH_3OH(l) + 1.5O_2(g) . 2H_2O(l) + CO_2(g)$, $E. = 1.213V$ (3)

Primary components of a fuel cell are an ion conducting electrolyte, a cathode, and an anode. Taken together these three components are often referred to as the membrane electrode assembly or MEA. This is a simple single cell fuel cell. Several simple single cell combined make up a more useful MEA. In the simplest example, a fuel is brought into the anode compartment and an oxidant, typically oxygen from the air, enters the cathode compartment. Direct chemical combustion is prevented by the electrolyte that separates the fuel from the oxidant. The electrolyte serves as a barrier to gas diffusion, but lets ion migrate across it. The electrochemical reactions are essentially as follows: first, a methanol molecule's carbon-hydrogen, and oxygen-hydrogen bonds are broken to generate electrons and protons; simultaneously, a water molecule's oxygen-hydrogen bond is also broken to generate an additional electron and proton. The carbon from the methanol and the oxygen from the water combine to form carbon dioxide. Oxygen from air (supplied to the cathode) is simultaneously reduced at the cathode. The ions (protons) formed at the anode migrate through the interposing electrolyte and combine with the oxygen at the cathode to form water.

Electrode :With pure platinum, carbon monoxide is the thermodynamic sink and will poison the surface if not removed. Research has shown that the bifunctional mechanism of a platinum-ruthenium catalyst is best because methanol dehydrogenates best of platinum and water dehydrogenation is best facilitated on ruthenium. Most commonly, platinum nanoparticles on carbon are utilized for both the anode and cathode. In direct methanol fuel cells a platinum-ruthenium (PtRu) alloy in a 50:50 molar ration is used at the anode. Ruthenium has the ability to electro-oxidize carbon monoxide that is adsorbed onto the platinum.

It is the anode catalyst that provides the foundation for converting the chemical energy of the fuel into electrical energy. Platinum (Pt) is the best anode for hydrogen oxidation, but in the presence of methanol, CO, formed as a reaction intermediate, irreversibly absorbs to the Pt surface, rapidly lowering its activity. Pt/ Ru bifunctional catalysts are presently the most active for methanol oxidation, with ruthenium (Ru) believed to serve the role of removing the absorbed carbon monoxide as carbon dioxide gas. This is shown in the equation below.

$\text{Ru-OH} + \text{Pt-CO} \rightarrow \text{Ru} + \text{Pt} + CO2 + H + + e-$

Direct methanol fuel cells do not have many of the fuel storage problems typical of some fuel cells since methanol has a higher energy density than hydrogen—though less than gasoline or diesel fuel. Methanol is also easier to transport and supply to the public using our current infrastructure since it is a liquid, like gasoline.

Direct Ethanol Fuel cell (DEFC):

The specific energy of ethanol is 8.03 kWh/ kg, compared to 32.8 for hydrogen . Taking the density of the fuel into account, however, the energy density of ethanol is 6.28 kWh/ L (0.18

kWh/ L1 for compressed hydrogen). The DEFC theoretical energy efficiency under reversible conditions, defined as the ratio between the electrical energy produced and the heat of combustion at constant pressure, is 97%. Under working conditions, however, the cell voltage, severely affected by the current density, is much lower and thereby also the practical efficiency attainable for the DEFC. More realistically, working at 0.5 V and 100 mA/ cm^2 with complete oxidation of ethanol to CO_2, result in an efficiency of 40%, and hence the DEFC is in the same range as a diesel ICE.

The electrochemical reactions are given below.

Anode reaction: $CH_3CH_2OH + 3H_2O$ ®. $2CO_2 + 12H^+ + 12e^-$ ($E_a = 0.084$ V versus SHE)

Cathode reaction: $3O_2 + 12H^+ + 12e^-$. ® $3H_2O$ ($E_c = 1.229$ V versus SHE)

Overall reaction: $CH_3CH_2OH + 3O_2$. ® $2CO_2 + 3H_2O$ ($E_{cell} = 1.145$ V)

Microbial Fuel cell:

When micro-organisms consume a substrate such as sugar in aerobic conditions they produce carbon dioxide and water. However when oxygen is not present they produce carbon dioxide, protons and electrons.

Anode Reaction : $C_{12}H_{22}O_{11} + 13H_2O \dashrightarrow 12CO_2 + 48H^+ + 48e^-$

Cathode Reaction : $12O_2(g) + 48H^+ + 48e^- = 3H_2O(l)$, $E_c = 1.229V$

A biological fuel cell is a device that directly converts biochemical energy into electricity. The driving force of a biological fuel cell is the redox reaction of a carbohydrate substrate such as glucose and methanol using a microorganism or an enzyme as catalyst. Working principle is similar to that of chemical fuel cells. The main differences are that catalyst in the biological fuel cell is microorganism or enzyme, therefore noble metal is not needed, and its working conditions are mild: neutral solution and room temperature. For example, complete oxidation of one gram of methanol by an enzyme gives theoretically 5000 mAh of electric energy.

Glucose Fuel cell:

Glucose is produced in abundance from both naturally occurring plants and industrial processes. Compared to alcohol fuels, such as methanol and ethanol, which have been used widely in direct oxidation fuel cells (DOFCs), glucose is nontoxic, non-flammable, odourless and renewable. These properties make glucose an attractive fuel for various applications, particularly for portable electronic devices.

The electrochemical oxidation of glucose fuel is as follows:

C6H12O6 + 2OH − → C6H12O7 + 2e − + H2O, E0an = 0.853 V…(1)

12O2 + 2e − + H2O → 2OH −, E0cath = 0.403 V…. (2)

Overall: C6H12O6 + 12 O2 → C6H12O7, E0cell = 1.256 V…. (3)

Energy ΔG = nFE = = 2 X 23061 X 1.256 = 57929.23 cal = 243.30 K joules/ mole = 1.35KJ/ gm.

Where n = No of Electrons ,F = Faraday's constant. E = Cell Potential.

It is seen from above reaction 243KJ energy is produced from 1 mole of glucose

Direct glucose alkaline fuel cells (DGAFCs) that directly produce electricity from glucose seem a potential choice for broader applications.

Electrode : Generally it is important to develop low cost catalysts with high catalytic activity towards glucose oxidation. Noble metal based catalyst, such as, Pt, bi-metallic catalysts of Pd-Pt , Ag-Au [catalysts are reported for glucose oxidation in alkaline media. Manganese oxide (MnO2) is also reported as a glucose oxidation catalyst and exhibits reasonable activity for oxidation of other carbohydrates, such as fructose. The low cost of MnO2 could provide the possibility of reducing noble metal content for glucose oxidation catalysts.

2.2 Fuels in Fuel Cell

Fuels in fuels are those electrochemicals which can be ionized easily on the electrocatalytic surface . The common fuels used in fuel cell are depicted below.

i. Hydrogen gas
ii. Methanol

iii. Ethanol
iv. Glucose

2.2.1 Hydrogen

The most popular fuel is the Hydrogen gas which can be obtained in pure form from different resources viz. electrolysis of water, steam-methane reforming , biomass: green algae produce hydrogen gas. The main advantage of using hydrogen as fuel is that the product of oxidation is pure water which can be used for drinking, washing and cultivation of agriculture products. H2 is electro oxidized on electro catalytic anode Because pure hydrogen does not occur naturally on Earth in large quantities, it takes a substantial amount of energy in its industrial production. There are different ways to produce it, such as electrolysis and steam-methane reforming process. In electrolysis, electricity is run through water to separate the hydrogen and oxygen atoms. This method can use wind, solar, geothermal, hydro, fossil fuels, biomass, nuclear, and many other energy sources Obtaining hydrogen from this process is being studied as a viable way to produce it domestically at a low cost. Steam-methane reforming, the current leading technology for producing hydrogen in large quantities, extracts the hydrogen from methane. However, this reaction causes a side production of carbon dioxide and carbon monoxide, which are greenhouse gases and contribute to global warming. Electrolysis of water produces pure hydrogen , Electrolysis involves passing an electric current through water to separate water into its basic elements, hydrogen and oxygen. Hydrogen is then collected at the negatively charged cathode and oxygen at the positive anode. The one disadvantage of electrolysis is that significant amounts of electrical energy are needed for the process. So the energy synthesis will be expensive.

2.2.2 Methanol

Methanol is a liquid fuel which may be made from hydrocarbon or renewable resources, in particular natural gas and biomass respectively. It can also be synthesized from CO2 (carbon dioxide) and hydrogen. Historically methanol was produced by pyrolysis of woody biomass and was called wood alcohol. The biomass is gasified and the resulting synthesis gas, a mixture of CO, H_2 and CO_2 . During synthesis the following reactions occur:

$$CO + 2H_2 \longleftrightarrow CH_3OH$$

$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_20$

$CO_2 + H_2 \longleftrightarrow CO + H_20$

The formation of CH3OH is exothermic and is favoured by high pressures and low temperatures. Direct oxidation of Methane also gives methanol : $2CH_4 + O_2$ $2CH_3OH$

2.2.3 Ethanol

Ethanol is another popular liquid fuel fuel for fuel cell. Ethanol is produced both as a petrochemical, through the hydration of ethylene and, via biological processes, by fermenting sugars with yeast. By petrochemical process, reaction is carried out in the presence of high pressure steam at 300 ° C (572 ° F) where a 1.0: 0.6 ethylene to steam ratio is maintained.

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

The catalyst is most commonly phosphoric acid, adsorbed onto a porous support such as silica gel. It can be also produced by reacting ethylene with concentrated sulfuric acid to produce ethyl sulfate, which was hydrolyzed to yield ethanol and regenerate the sulfuric acid.

2.2.4 Glucose Fuel

Glucose is extracted from cane sugar and other fruits juice . The extractant is purified to glucose fructose and other sugar products. It is also produced from woody biomass by acid and enzymatic hydrolysis. It is also a renewable fuel. Glucose is a main fuel in the human body. Energy produced from the oxidation of glucose, supplies the total energy requirement of our body for functioning the human organs and doing all of our daily activities. The food we eat is converted to simple glucose type of molecules by metabolism. The glucose is normally contained in the blood and human being survives on energy synthesis through the consumption of the fuel glucose.

2.3 Anode and Cathode: High Electrocatalytic Materials

For energy conversion through fuel cell, electrodes having high electro catalytic properties are needed to be developed. A good anode material should have the electro catalytic property for fast electrochemical oxidation along with good electrical conductivity, low polarization resistance, chemical stability and anti-corrosion property. A cathode material on other hand should have capacity to capture and transfer electron rapidly with high redox potential besides low polarization resistance. For fuel cell electrodes, Pt and Pt based alloys make high energetic good electrodes. Platinum is already found as good electro-catalytic material in laboratory scale for many fuel cell applications but due to its high cost, a non platinum based low cost electrode is the urgent need of research. There is also a bad effect of using platinum. Pt is also extremely susceptible to poisoning by CO and halides[2]. Several oxides and metal alloys have been found to show good electro catalytic properties. Materials such as CoTi[3] , PbO2[4] , TiO2[5] and β-MnO2[6] , Ni-Co , Ni- Co-Fe show very encouraging results for application in fuel cell electrodes.

2.3.1 Precious Materials for fuel cell

For energy conversion through fuel cell, electrodes having high electro catalytic properties are needed to be developed. Platinum is already found as good electro-catalytic material in laboratory scale for many fuel cell application but due to its high cost, a non platinum based low cost electrode is the urgent need of research. There is also a bad effect of using platinum. Pt is also extremely susceptible to poisoning by CO and halides [5]. CO and halides are strongly adsorbed on the Pt surface and the active sites are blocked from further catalysis, resulting in a dramatic decrease in efficiency and overall performance of any redox reaction. To limit the poisoning by CO, some CO-catalyst [6-9] like Ru, Sn, Au, W, Mo, Os, Re, Rh, Pd, Pb, Bi are added to promote CO oxidation. In fuel cell development, Platinum-based nano materials with high surface areas have been receiving increased attention due to their unique properties and a number of impressive applications. So our aim is to develop Non-Pt based electro catalysts having good electro-catalytic property for low cost fuel cell.

2.4 Synthesis of electrode materials.

Details of electrodeposition:

Electrodeposition is performed in a liquid solution called an electrolyte, otherwise referred to as the "plating bath". The bath is a specially designed chemical solution that contains the desired metal (such as gold, copper, or nickel) dissolved in a form of sub-microscopic metallic particles (positively charged). In addition, various substances (additives) are introduced in the bath to obtain smooth and bright deposits. The object that is to be plated is submerged into the electrolyte (plating bath). Placed usually at the centre of the bath, the object that is to be plated acts as a negatively charged cathode. The positively charged anodes complete the electric circuit; those may be at opposite edges of the plating tank, thus causing film deposit on both sides of the cathode. A power source which providing the necessary current. This type of circuit arrangement directs electrons into a path from the power supply (rectifier) to the cathode. Now, in the bath the electric current is carried largely by the positively charged ions from the anode(s) toward the negatively charged cathode. This movement makes the metal ions in the bath to migrate toward extra electrons that are located at or near the cathode's surface outer layer.

Finally, by way of electrolysis the metal ions are removed from the solution and are deposited on the surface of the object as a thin layer. It is this process to which we refer as "electrodeposition"

Electrodeposition or electrochemical deposition (of metals or alloys) involves the reduction of metal ions from aqueous, organic, or fused salt electrolytes. In its simplest form the reaction in aqueous medium at the cathode follows the equation (1)

Cathode half-cell reaction: M+n + ne ==> M (1)

(Eo value depends on Metal, as for example $E^{\circ}_{Ni+2/Ni+}$=.250V , $E^{o}_{Fe+2/Fe}$=.440V,) with a corresponding anodic reaction. The anode material on either be the metal to be deposited (in this case the electrode reaction is electro dissolution that continuously supplies the metal ions) or the anode can be an inert (graphite or lead) material and the anodic reaction is oxygen evolution (in this case the plating solution is eventually depleted of metal ions).

Anode half-cell reaction: H2O =2H +1/202+2e Eo=1.23V (2)

The deposition reaction presented in Equation (1) is a reaction of charged particles at the interface between a solid (metal) electrode and a liquid solution. The two types of charged particles that can cross the interface are metal ions "M+" and electrons "e".

In practical electrodeposition processes under the influence of an applied potential, rearrangement of ions near the electrode surface results in an electrical double layer called the Helmholtz double layer, followed by the formation of a diffusion layer as shown in Figure 2.3 These two layers are referred as the Gouy-Chapman layer. The processis as follows:

(1) **Migration**: The hydrated metal ions in the solution migrate towards the cathode under the influence of impressed current as well as by diffusion and convection.

(ii)**Electron transfer**: At the cathode surface, a hydrated metal ion enters the diffused double layer where the water molecules of the hydrated ion are aligned.

Then the metal ion enters the Helmholtz double layer where it is deprived of its hydrate envelope.

(iii).The dehydrated ion is neutralized and adsorbed on the cathode surface.

(iv). Nucleation and growth process of the adsorbed metal lattice on the cathode surface takes place.

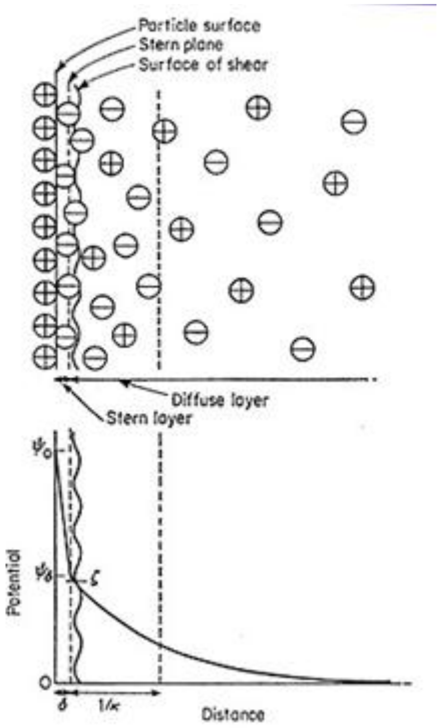


Figure 2.3: Schematic representation of electrical double layer.

The reduction of a metal, which occurs during the plating process, has been generalized as Equation (1) for a metallic ion. Obviously, to reduce one mole of a given metal "n" moles of electrons are required. That is, the total cathodic charge used in the deposition "Q" (coulomb) is the product of the number of gram moles of the metal deposited "m", the number of electrons taking part in the reduction "n", Avogadro's number "N" (the number of atoms in a mole), and we electrical charge per electron "Qe" (coulomb). Thus, the following equation gives the charge required to reduce "m" mole of metal:

$Q = m\ n\ Na\ de$

Now the product of the last two terms in this equation is the "faraday constant”(F)

Therefore ,the number of moles of metal reduced by charge "Q" can be obtained as:

$m=Q/(n\ F)$ (3)

other hand, the total charge used in the deposition can be obtained as the product

of the current "T" (ampere) and the time of deposition "t" (second) if the deposition current is held constant. Or, if the current varies during the deposition:

$Q=\int Idt$ (4)

So,the number of moles deposited can be calculated as:

$M=1/(nF) \int Idt$ (5)

The weight of the deposit "w" (gram) can now be obtained by multiplying Equation [5] with the atomic weight "Mw" of the deposited metal. Finally, to calculate the thickness of the deposit, we have to use the density of the metal "D" ($gram/cm^3$):

$D=w/V = w/(A\ T)$ (6) where "V" is the volume of the deposited metal in cm", "A" is the area of the deposit in cm2, and "T" is its thickness in cm. Solving for thickness, using Equations [5] and [6] we have the useful practical expression:

$T=w/AD=Mw/(nFAD) \int Idt$ (7)

As mentioned above, if the current was held constant during the deposition, the inegral in Equation [7], can be replaced by the simple product of current andtime "Ixt".

2.4.1 Electrodeposition Method .

Metals or oxides can be deposited at cathode or anode from the cations or anions in the electrolyte by passing a desired amount of current at a predetermined potential. For Cu deposition at the cathode the reaction is :

Cathode $Cu^{++} + 2e^{-} = Cu$ at potential E_{Cu}

There should be a corresponding anodic reaction to balance the electron released. Under acidic/ neutral condition:

Anode $2H_2O = 2H^{+} + O_2 + 2e^{-}$

If MnO_2 is deposited at the anode, the reactions are

Anode $Mn^{2+} + 2H_2O = MnO_2 + 4H^{+} + 2e^{-}$

Cathode $2H^{+} + 2e^{-} = H_2$

The parameters which control the characteristics of electrodeposition are as follows.

2.4.2 Applied potential E .

The applied Potential is the sum of equilibrium potential E_{eq}, overvoltage(n), due to polarization of the electrode and IR drop due to the resistance of the electrolyte.

$$\mathbf{E = E_{eq} + n_{act} + n_{con} + IR_{elyt}}$$

Where n_{act} = Overvoltage due to activation polarization or charge transfer electrode reaction.

n_{con} = Overvoltage due to concentration polarization or mass transfer process by diffusion through the electrolyte

R_{elyt} = Resistance of the electrolyte .

Generally for electrodeposition, the conductivity of the bath is made very high and the 3rd term of the equation may be neglected.

2.4.3 Equilibrium potential (E_{eq}).

Eeq is expressed by Nernst equation.

For a metal M :

$$M^{++} + 2e \longleftrightarrow M$$

$$Eeq = E^{o}_{M} + 2.33RT/(nF) \log[M^{++}]$$

Where E^0_M is the standard electrode potential F = faraday, n = no of the electrons involved .

2.4.4 Activation Overvoltage(n_{act})

It is given by Tafel's equation as follows

$n_{act} = \pm n\log(i/i_o)$.

where n is the Tafel's slope, i_0 is the exchange current densiy.(See fig 2.3)

For anodic reaction $n_{act,a} = \pm n_a\log(i_a/i_o)$

For Cathodic reaction $n_{act,c} = \pm n_c\log(i_c/i_o)$

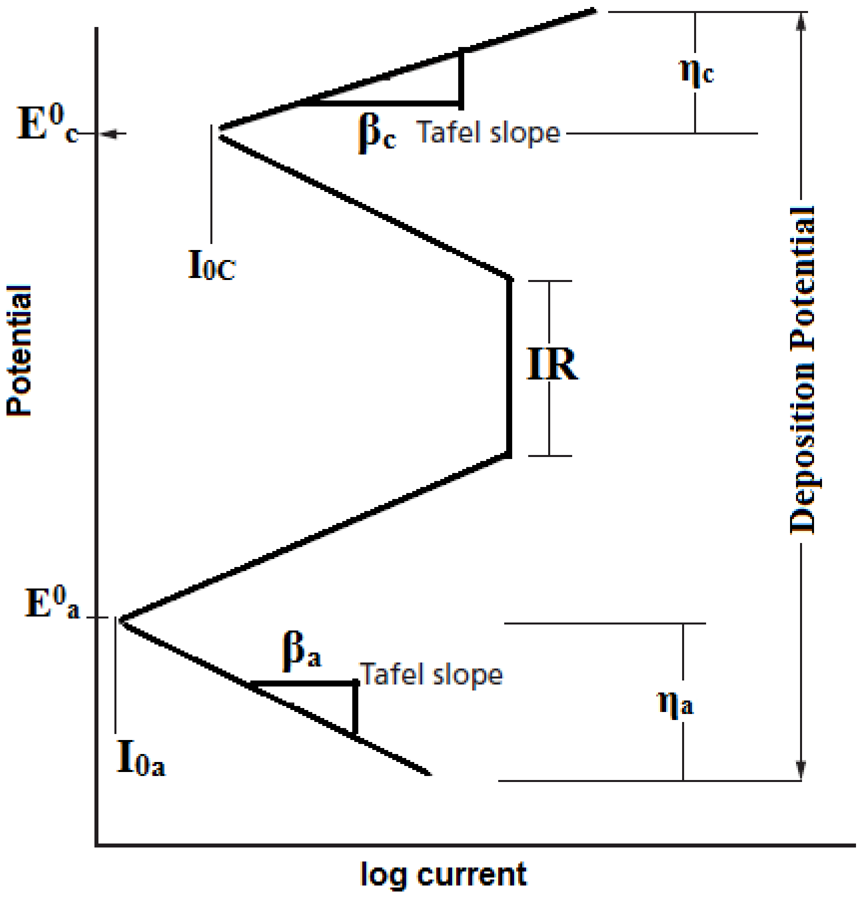


Fig 2.3 Activation polarization by electrodeposition.

2.4.5 Concentration Overvoltage(n_c).

The concentration of the reducing species in the electrolyte near the cathode varies as shown in fig. 2.4, with a stagnant diffusion barrier, known as Nernst diffusion layer . Concentration of M^{++} ions deceases from the bulk solution towards the metal-solution interface. The speed at which electron is transported at the cathode is much greater than the speed of diffusion of ions towards the electrode surface. The concentration polarization arises due to non availability of the ions, to be reduced by waiting electrons at the cathode. When the concentration of the ion at the electrode surface becomes zero , it is the limiting case and polarization approaches negative infinity . The current corresponding to this situation is the limiting current density i_L .

n_{coc}=2.33RT/nF log(1-i/iL)
iL=DnFCB/d

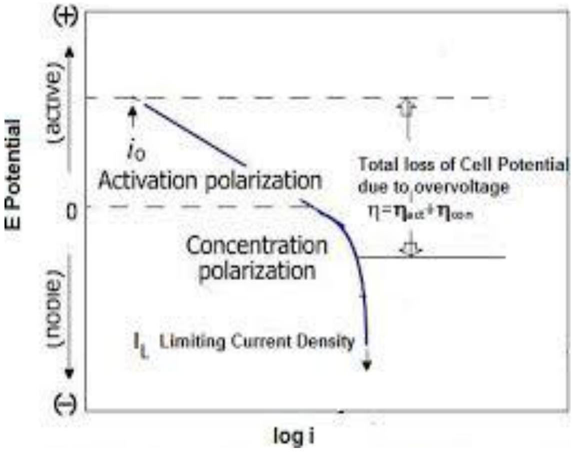


Fig 2.4 concentration polarization.

2.4.6 Combined Overvoltage(n).

An electrode reaction may be charge transfer control or combined charge and mass transfer controlled where both activation and concentration polarizations are involved. For the charge transferred controlled, it is governed by Bulter-volmer relationship.

$n = n_{act} + n_{coc}$

$n = n\log(i/i_o) + 2.33RT/nF \log(1 - i/i_L)$

2.4.7 Applied current

The current decides the rate at which electron is made available at the cathode for discharge reaction or the electron is taken out from the anode, for anions formation. So the rate of electrodeposition is directly proportional to the current. But the current is related to potential through the polarization equation . So higher is the current , more is the overvoltage.

Depending on the current, the electrodeposition may be under activation potential control or diffusion polarization control.

Properties of deposited film:

(i) **Adhesion**: As one of the most important requirements, adhesion is mostly dependent upon substrate. For proper adhesion, the substrate must be thoroughly cleaned and free of any surface films.

It is desirable that the substrate and the deposited metal interdiffuse with interlocking grains to give a continuous interfacial region. Alloy formation by the interdiffusion of the substrate and the deposited metals provides good adhesion

(ii)**Mechanical properties**: Mechanical properties of the electrodeposited film depend to a considerable extent on the types and amounts of growth-inhibiting substance at the cathode surfaces. The purpose of using a growth-inhibiting substance is to obtain finegrain structure of the deposited film, in which the grain boundaries act as the main obstacles to dislocation motion, leading to a higher yield strength and hard surface.

Hardness of the deposited film can also be increased by introducing lattice strain through incorporating impurities into the film-growth process. Electroplating processes frequently result in the development of internal stresses. The reasons for internal stresses relate to coalescence of three-dimensional, epitaxial crystallites, dislocation configurations, hydrogen incorporated into the crystal lattice, or other factors.

(iii)**Brightness**: Brightness of deposited film is critical for decoration application .The brightness of thin deposited films depends on the surface finish of the substrate.

is critical for decoration applications. Thicker bright deposited films are produced by additional agents in the plating solution which result in elimination of crevices. The addition agents are mostly organic compounds such as dextrose, saccharine, lactose, formalin, citrates,
tartarates, etc. However, most good brighteners are sulphur compounds, especially thio-urea and its derivatives and organic sulphonic acids.

Brightening agents are foreign inclusions in the deposited film. Over dosage of these additives can cause brittleness and lead to cracks and stripping off of the
deposited film from the substrate.

Applications:

Its applications are mainly in the following five groups:

(i) **Decoration**: Coating a more expensive metal onto a base metal surface in order to improve the appearance. Applications are jewellery, furniture fittings, and builders' hardware etc.

(ii) **Protection**: Corrosion-resistant coatings such as chromium plating of automobile parts and domestic appliances, zinc and cadmium plating of nuts, screws and electrical components.

(iii)**Electrocatalyst**: Metallic or alloy coating on conductive surface affords catalytic behaviour for oxidation of alcohol in fuel cell (as for example Pt,Pt-Ru , Ni-Co, Ni-Fe-Co alloy coating on conductive surface.)

(iv)**Electroforming**: Manufacture of sieves, screens, dry shaver heads, record stampers, moulds and dies.

(v)Enhancement: coating result improved electricaland thermal conductivity, solderability, reflectivity etc.

2.5 Electrochemical and material characterization of electrode material.

The route to the development of electrode materials for high energetic and high efficiency fuel cell is synthesis of materials and the performance of them by electrochemical and materials

characterization. After the right electrodes materials have been found, the fuel cell is fabricated and performance test of the fuel cell is carried out for final arrival of them for domestic and commercial applications. The electrochemical characterization broadly consists of the following testing i. Cyclic Voltammetry;
ii. Chronoamperometry;
iii Potentiodynamic Polarization;
iv. Electrochemical Impedance Spectroscopy (EIS);
The material characterizations are analysis of constituents metals, alloys , oxides etc on electrode surface by X ray diffraction techniques. The morphology of the surface deposit is studied by electron microscope. The battery performance test is carried out : Discharge performance vii. Potential vs current characteristics under load . The fuel cell characterization is done by Discharge performance vii. Potential vs current characteristics under load . The cyclic voltammetry and chronoamperometry tests are done to achieve high and stable current at redox potential so that the battery yields onload high specific energy. The potentiodynamic polarization and electrochemical impedance spectroscopy tests are performed to develop electrodes with low anode and Cathode overpotentials for anodic and cathodic reactions as well as high hydrogen overpotential at cathode and high oxygen overpotential at anode and low IR drop, that is high electrolyte conductivity. So the net cell voltage Ecell, net, given by equation is high. Electrodes synthesized by nanomaterial coating are characterized for surface morphology by XRD and electron microscopy. The E-I-characteristics of the fabricated fuel cell are studied by varying external load.

2.5.1 Cyclic voltammetry (CV)

Fundamentals of cyclic voltammetry

CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode such as a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). The controlling potential which is applied across these two electrodes can he considered an excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform as shown in Figure (2.5). This triangular potential excitation signal sweeps the potential of the electrode between two values, sometimes called the switching potentials. The scan rate, as reflected by the slope, is 50 mV/s. A second cycle is also indicated in figure (2.5). Single or multiple cycles can be used. The. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis) because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This is helpful in understanding the fundamentals of the technique.[7]

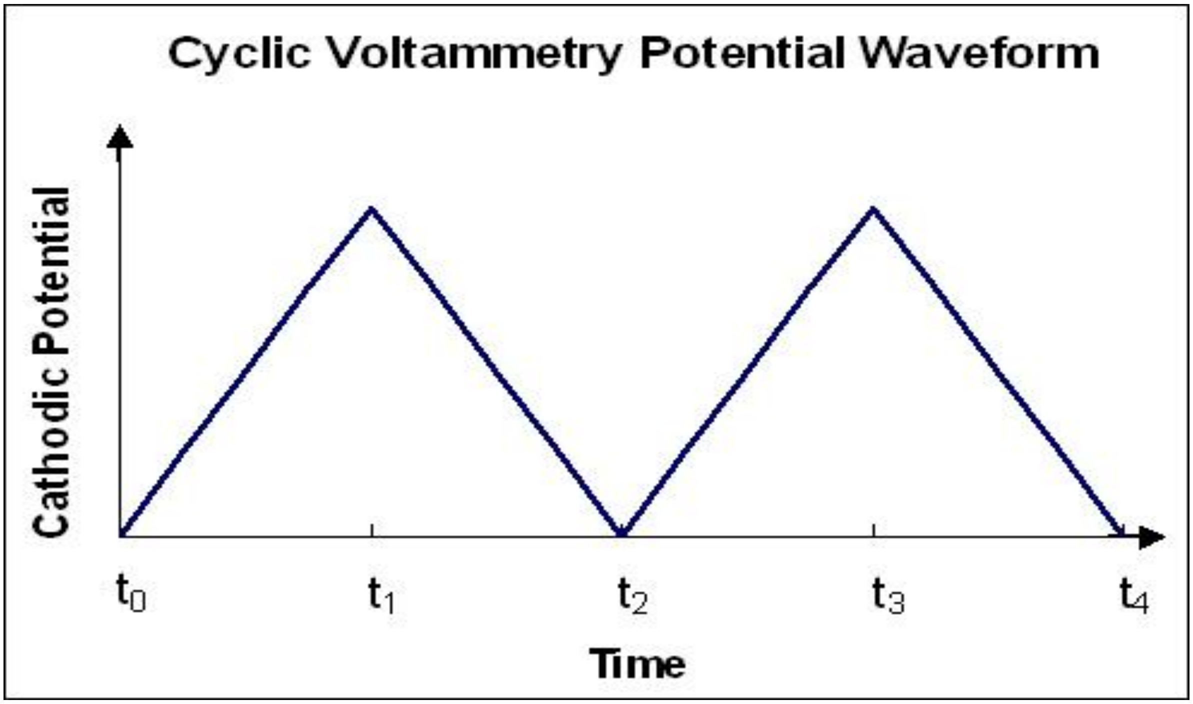


Fig 2.5 Cyclic voltammetry potential waveform.

The cyclic voltammetry test of the electrode in anodic or cathodic solution is done to achieve high and stable current at redox potential so that the cell yields onload high specific energy. In CV the potential is scanned, starting from a prefixed potential well below the potential for cathodic reduction of the half cell reaction to that over the potential of anodic oxidation of other half cell reaction. The potential of the working electrode is measured against a reference electrode which maintains a constant potential, and the resulting applied potential produces an excitation signal. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scans .The current is first observed to peak at Epc(with value ic) indicating (fig 2.6) reduction of species and then drops due to depletion of the reducing species from the diffusion layer. This cycle can be repeated, and the scan rate can be varied. The slope of the excitation signal gives the scan rate used. In a slow voltage scan rate the diffusion layer will grow much farther from the electrode in comparison to a fast scan. The higher is the peak current Ia or Ic , the faster is rate of oxidation or reduction. The area under the curve gives the energy produced. The curve shows a peak current density at a fixed potential, indicating oxidation or anodic reaction at that potential. Higher currents indicate better battery materials. The area within the enclosed curve is significant. It indicates the energy content of the fuel. So a bigger area is wanted for future fuel cell. Fig 2.6 cyclic voltammetry excitation and resulting voltammogram .

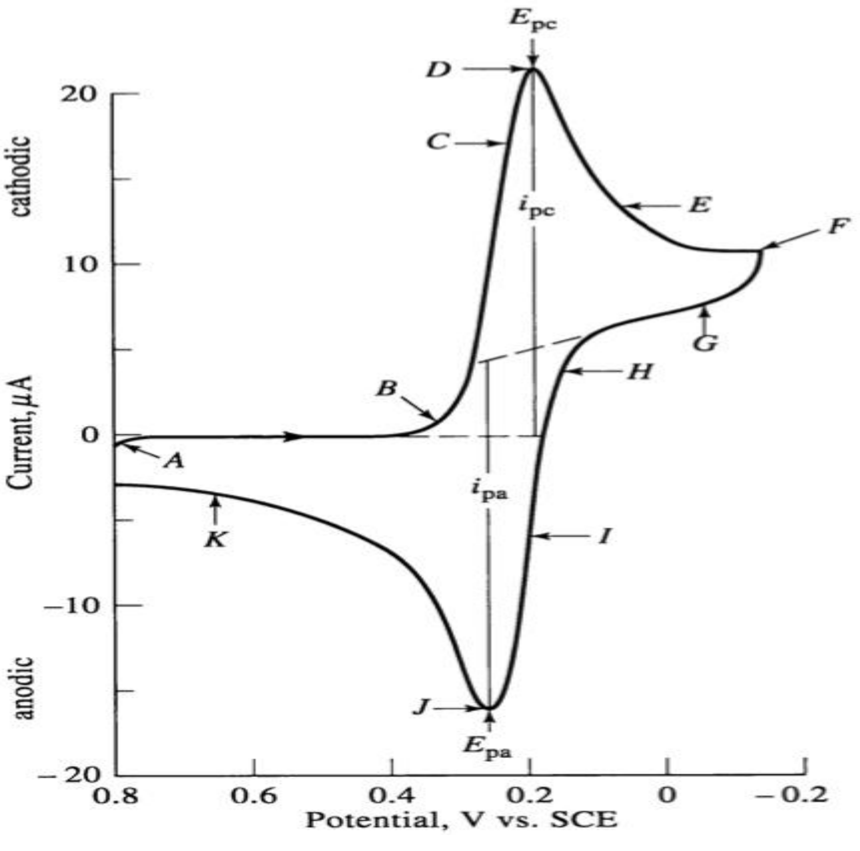


Fig 2.6 cyclic voltammetry excitation and resulting voltammogram.

2.5.2 Chronoamperometry.

It is conducted to study I = f(t) at different fixed potentials preselected around the anodic or cathodic potential. Such measurement gives us additional qualitative and quantitative information about the electrolyte composition, speed of electrode processes and chemical reaction taking place at the electrodes and in electrolyte. Chronoamperometric curves should be registered at potentials exceeding overpotential value.

To investigate the Chronoamperometry study to find out the nature of steady state current. Fig. (2.7) shows the chronoamperometry study for ethanol solution on electro coated Ni-Cu substrate at different potentials. It is seen that the current decreases initially and reaches a steady state within about 100 second and remains at the steady state current for a long duration. So it gives an idea that this particular electrode can be used for a fuel cell for steady state energy.[8]

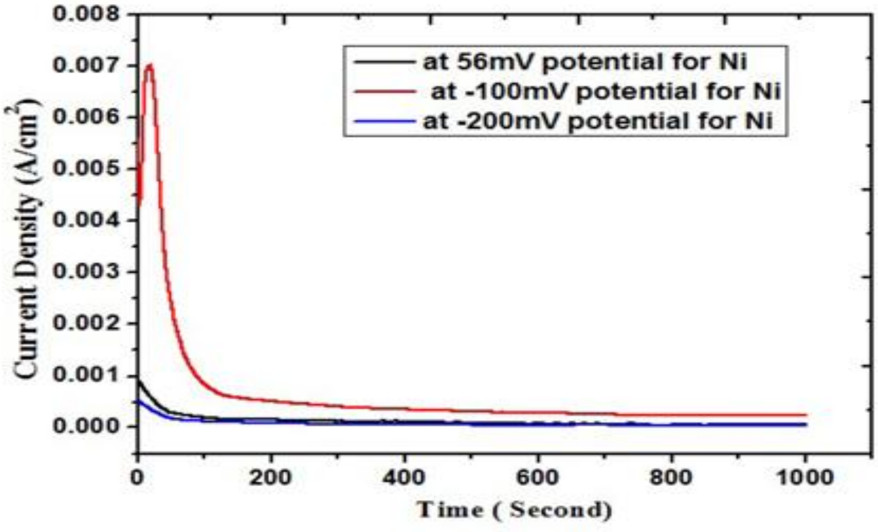


Fig 2.7 *Chronoamperometry curve of ethanol oxidation reaction on Ni-Cu electrode at different potentials.*

The potentiodynamic polarization tests are performed to develop electrodes with low anode and Cathode overpotentials for anodic and cathodic reactions as well as high hydrogen overpotential at cathode and high oxygen overpotential at anode and low IR drop, that is high electrolyte conductivity Here the potential is scanned from cathodic to anodic side and the corresponding current is recorded. From the graph and experimental data, all electrokinetic parameters such as Tafel slope, exchange current density, limiting current density, overpotential etc are determined . Depending on applied potential/ current, an electrode process can be charge transfer controlled or mass transfer controlled. The polarization curve thus guides the right selection of electrode material for a fuel cell. The exchange current determination helps to give information on electrochemical properties of the substrate on which the anodic/ cathodic reaction takes place. A substrate with high exchange current density shows increased rate kinetics of the redox reaction. For example it is found that an electrode substrate prepared or modified by nanodeposition has a very high exchange current density and yields electrode process at a very high rate .

Potentiodynamic polarization tests are carried out to compute the electro kinetic parameters of the developed electrodes. Electro kinetic parameters, i.e. exchange current density and polarization resistance are calculated using Tafel equation [9-11] . Fig. (2.8)depicts the polarization curves of Ni-CeO_2-Cu electrode for comparison the curve for Pt and Cu foil has also been superimposed. While the nature of the all the curves same, the curve for Ni-CeO_2-Cu is the most right hand side curve that implies, it is giving the higher current for all over the potentials. It is to be noted that each of the curves, there is a current hump just above the reversible potential (E_{cell} reversible in the oxidation region). This current hump implies oxidation of ethanol on the different substrate materials [12,13] . The higher current for Ni - CeO_2-Cu electrode indicates that it is the best performing electrode substrate.

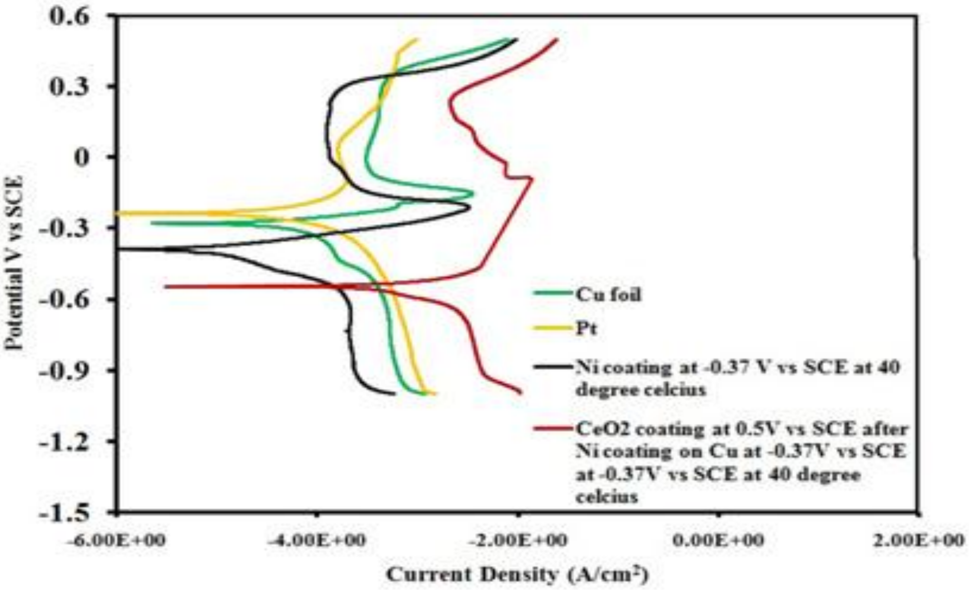


Fig 2.8 *Polarization study of bare Cu, Pt, Ni-Cu and Ni-CeO_2-Cu electrodes in 1M ethanol+1M KOH solution.*

2.5.3 EIS:

Electrochemical impedance spectroscopy is a perturbated dynamic characterization to obtain the electrochemical property. a sinusoidal test potential or current (ac potential or current) is applied to the sample to measure its impedance over a suitable frequency range. It is a powerful technique to investigate the electrochemical properties as well as equivalent electrical properties of materials. The electrochemical phenomenon occurring in the electrode surface which is immersed into the electrolyte, can be represented by an equivalent electrical RLC circuit. The measured impedance curve is generally fitted with an equivalent electrical model which gives us the unique equivalent electrical properties due to the electrochemical phenomena in the electrode-electrolyte interface and subsequently gives an idea about the behavior of the material or deposited film. [14]

Impedance is also a measure of the ability of a circuit to resist the flow of electrical current but unlike resistant. It is expressed as ‘Z’. It has two parts, real and imaginary. When the real part is plotted on the x axis and imaginary part is plotted on y axis , the resultant curve is ‘nyquist plot’. The resultant curve is a semicircle for the simplest circuit with one time constant.

Another type of representation method is the Bode Plot. The impedance is plotted with log frequency on the X-axis and both the absolute values of the impedance and the phase-shift on the Y-axis. Unlike the Nyquist Plot, the Bode Plot does show frequency information.

EIS plots are commonly analyzed by fitting to an equivalent electrical model. Most of the elements in the model are common electrical elements such as resistors, capacitors, and inductors.

The impedance value of resistor i.e resistance , R= E/I

The impedance of inductor i.e inductance, Z = wL

The impedance of capacitor i.e , z = 1/ wc

It can be said that the inductance is linearly proportional to the frequency while the capacitance is inversely proportional to the frequency.

Solution resistance is often a significant factor in the electrochemical impedance spectroscopy.of an electrochemical cell. solution resistance between the reference electrode and the working electrode must be considered when the equivalent circuit is made.

An electrical double layer may exist on the electrode electrolyte interface. This layer is formed as ions from the solution adsorb onto the electrode surface. The charged electrode is just separated from the charged ions by a very thin insulating space. So, eliminating the separation , double layer will behave like capacitance.

The change in potential from it's initial value is known as polarization. When the working electrode is polarized , it will result current to flow through electrode surface. the amount of the current is controlled by kinetics of the reactions , the diffusion of the ions present in the electrolyte solution. The factors which resists in the flow of this current in the process, is known as polarization resistance.

Diffusion also can create an impedance called a Warburg impedance. The impedance depends on the frequency of the potential perturbation. At high frequencies, the reactants can't diffuse fast so the Warburg impedance is small. At low frequencies , the value of Warburg is high.

Besides these parameters , coating capacitance may become a factor in the electrochemical impedance spectroscopy.

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element as defined below.

The impedance of a capacitor can be expressed as:

$$Z_{CPE} = \frac{1}{(j\omega)^{\alpha} Y_0}$$

where,

Y_0	= C = The capacitance
α	= An exponent equaling 1 for a capacitor

For a constant phase element, the exponent α is less than one.

Simplified Randles Cell

The Simplified Randles cell is one of most common cell models. It includes a solution resistance, a double layer capacitor and a polarization resistance.

The equivalent circuit for a Simplified Randles Cell is shown in Figure 2.9.

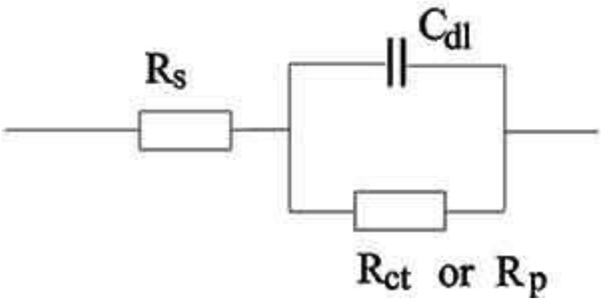


Figure 2.9. Simplified Randles Cell Schematic Diagram

Figure 15 is the Nyquist Plot for a typical Simplified Randles cell. The parameters in this plot were calculated assuming a 1 cm^2 electrode undergoing uniform corrosion at a rate of 1 mm/year.

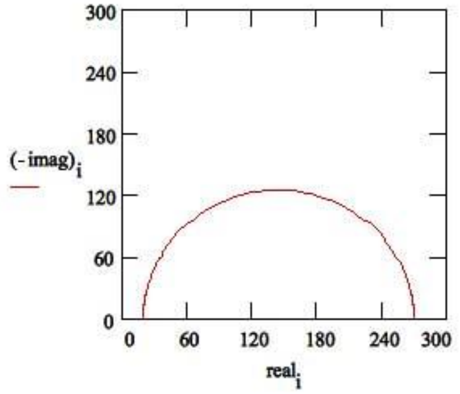


Figure 3.0 Nyquist Plot for Randle cell.

The Nyquist Plot for a Simplified Randles cell is always a semicircle.

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance.

Figure 16 is the Bode Plot for the same cell.

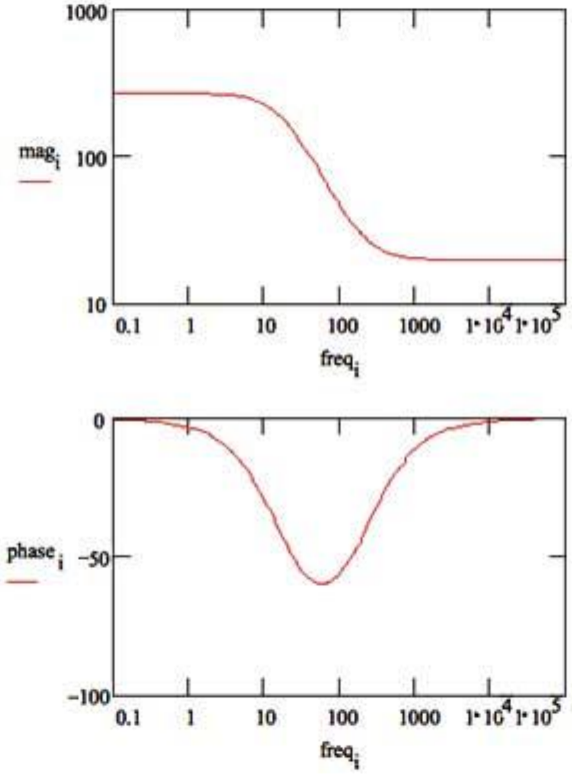


Figure 3.1. Bode Plot for 1 mm/year Corrosion Rate

Warburg model

Consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.

A Nyquist Plot for this cell is shown in Figure 3.2.

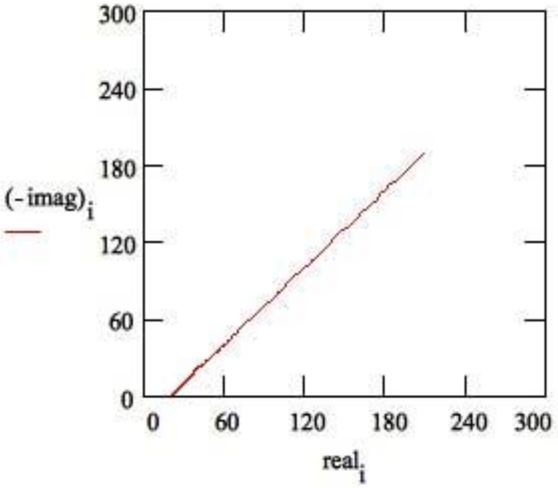


Figure 3.2. Nyquist Plot for a Warburg Impedance

The same data is plotted in the Bode format in Figure 18. The phase angle of a Warburg impedance is 45˚.

Adding a double layer capacitance and a charge transfer impedance, we get the equivalent circuit in Figure 19. Since there is no simple element to model a Warburg impedance, it isn't possible to construct a dummy cell that models the Randles Cell.

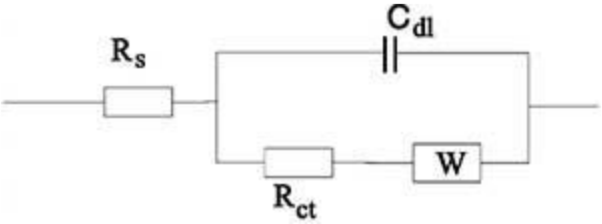


Figure 3.3 Randles Cell: Equivalent Circuit with Mixed Kinetic and Charge-Transfer Control

This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist Plot for this circuit is shown in Figure 3.4.

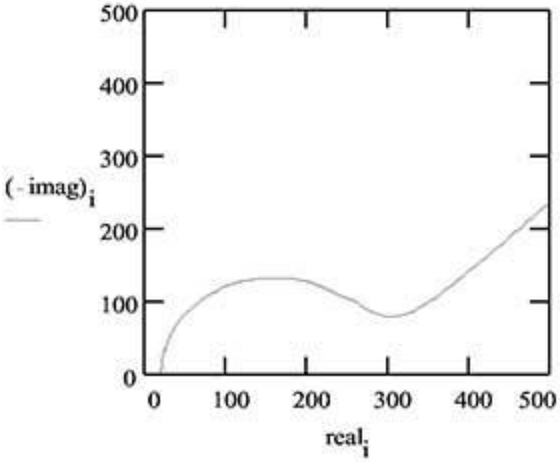


Figure 3.4. Nyquist Diagram for Mixed Control Circuit

The Bode Plot for the same data is shown in Figure 21. The lower frequency limit was moved down to 1 mHz to better illustrate the differences in the slope of the magnitude and in the phase between the capacitor and the Warburg impedance.

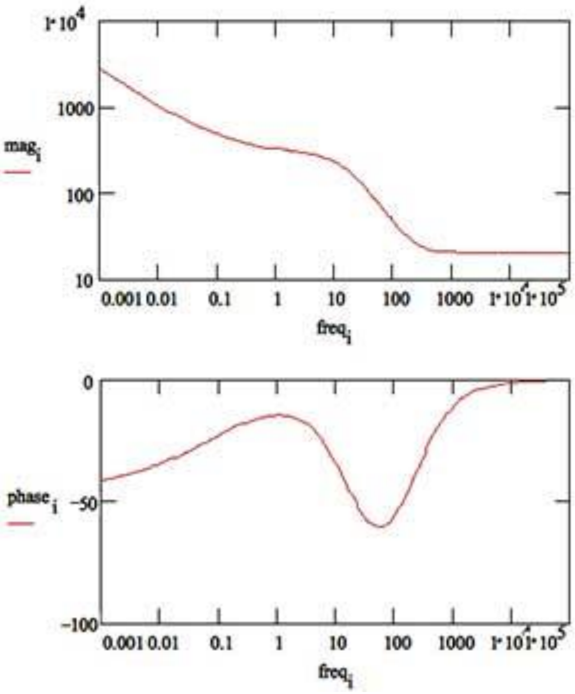


Figure 21. Bode Plot for the Mixed Control Circuit

2.6 Material characterization

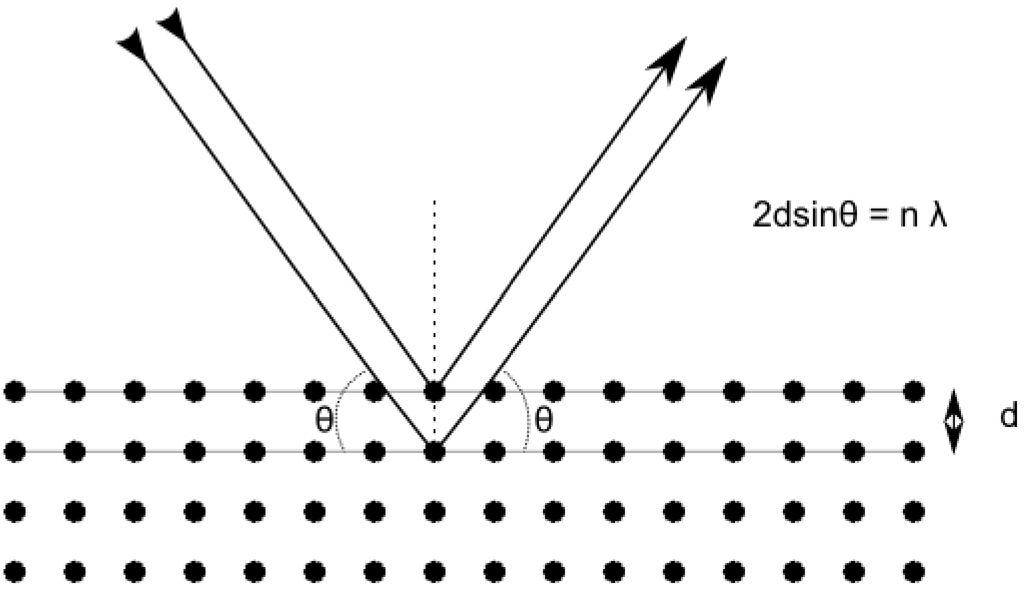
After finding the electrochemical properties of the developed material, it is necessary to understand the maerial's composition which is responsible for providing such properties. Material characterization is necessary to understand their composition and subsequent effect on the electrochemical characteristics.

2.6.1XRD:

X-ray diffraction technique is an analytical process to analyze the composition and their phases present on the material. Xrd is capable of providing the morphological informations such as unit cell dimensions , phases , grain size of crystalline material.

XRD is a non-destructive test for material characterization. The principle of xray diffraction is based on constructive interference of monochromatic x ray beams. First, x ray is generated from a cathode ray tube and filtered to create monochromatic ray. It is directed towards the sample with known angle. When it satisfies bragg's law , we got the constructive interference.

Bragg's law relates the wavelength of x-ray to the diffraction angle and the lattice spacing of the sample.



$n\lambda = 2d\sin\theta$

when this condition satisfies , constructive interference is achieved. X ray diffraction technique provides the peak for the different composition or phases present in the sample which is subsequently compared to the reference data. Thus the desired result is obtained from the x ray diffraction technique.

2.6.2 SEM :

Scanning electron microscopy is material characterization technique which provides the magnified view of the surface and the clear idea about the morphologies of the surface. it is also a non destructive method for material characterizing. A scanning electron microscope uses electron beams for imaging. It uses the electron that are reflected and knocked out by the sample surface. as the wavelength of electron is much shorter than visible light, it will provide better resolution than optical microscope.

A schematic representation of a SEM is illustrated in Figure 1 below. first, electrons are generated at the top of the column by the **electron source**. These are emitted from the source. They are then accelerated and attracted by the positively-charged anode.

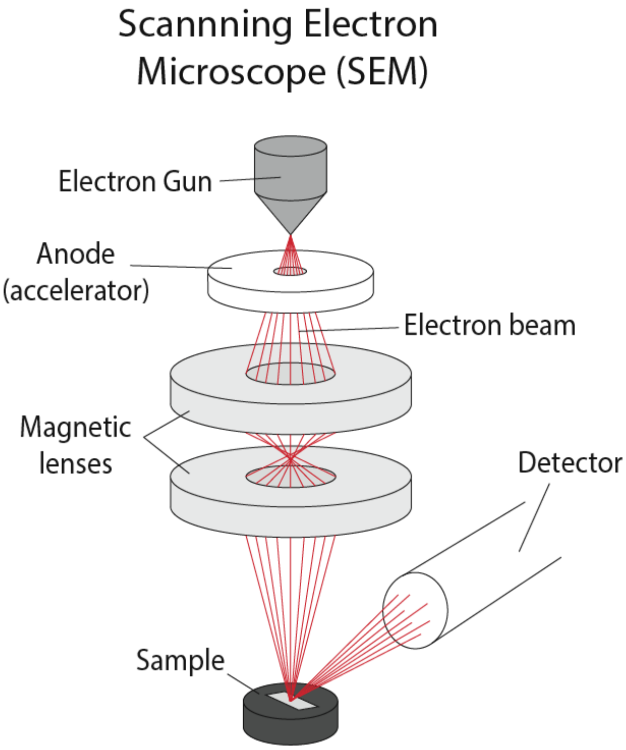


Figure 1: schematic representation of the basic SEM components

The entire electron column needs to be under vacuum because the path of electron can be diffracted easily by a minor magnetic field. The electron source is sealed inside a special chamber in order to preserve vacuum. Although the vacuum protects the electron source from vibration and noise, it also provide a high-resolution image. In the absence of vacuum, other atoms and molecules may be present in the column. Their interaction with electrons causes the electron beam to deflect and reduces the image quality.

As electrons cannot pass through glass, the lenses that are used in SEM are electromagnetic. When current passes through the coils inside the lenses , a magnetic field is generated. The sensitivity of electron to the magnetic field , the lenses are used to control the path of the electrons by changing the current.

The **condenser** lens is the first lens in the predetermined path of the electron. This lens converges the beam before the electron beam cone opens again and is converged again by the **objective** lens before hitting the sample. The condenser lens defines the size of the electron beam as well as resolution, while the objective lens leads the beam to focus onto the sample.

The scanning electron microscope’s lens system also contains the **scanning coils**, which are used to raster the beam onto the sample.

The electrons with high energy strike the sample. This interaction of electrons with sample results in the generation of many different types of electrons, photons or x ray emmision . SEM uses two types of electron for imaging such as secondary electron and back scattered electron.

Backscattered electrons are reflected back after elastic interactions between the electron beam and the sample. Secondary electrons are originated from the atoms of the sample from inelastic interactions between the electron beam and the sample.

BSE provides the information of the deeper regions as it comes from deeper regions of the sample whie Secondary electrons are originated from the surface. BSE can able to identify different material. The higher the atomic number , brighter the image of the materials by BSE. Secondary electron are used to form 3-D image of the sample surface.

The secondary and back scattered electrons are detected by different types of detectors. Solid state detectors are used to detect BSE. The detector is placed concentrically to the beam to maximize the collection of back scattered electron.

To detect secondary electron, the Everhart-Thornley detector is mainly used. Scintillator is used inside a Faraday cage, which is positively charged resuls in attracting the secondary electron. Secondary electron detector is placed at an angle to increase the efficiency.

CHAPTER 3

EXPERIMENTAL SETUP, MATERIALS AND METHODS

3 .Experimental Setup, Materials and Methods.

3.1 Raw Materials:

pure aluminum (99.9%) is used in many industry. Its high hardness, refractoriness and good thermal properties make it the material of choice for a wide range of applications.

Dimension- 1cm x1cm , Geometry- Plate.

3.2 Preparation of electrocatalytic electrodes.

3.2.1 Electrode pre-treatment of base metal Al:

This step is crucial before electrocatalytic electrodes surface preparation by electrodeposition .This significant adhesion of deposited surface with conductive object only achieve by removing contaminants and films from the substrate. At first the Aluminium surface was taken in rectangular from each of dimensions 3cmX1cm (thickness 0.50mm)

The surface of the Aluminium was prepared by following sequential steps-

(i) The edge of the rectangular shaped Aluminium was polished by emery paper (grain sizes were 180,120,1/0,2/0).

(ii) Degreased by acetone.

(iii) Electropolished in a solution of prechloric acid and ethanol.

(iv) Washed by double distilled water.

(v) Dipping in 1M KOH solution for some time.

(vi) Rinsing with double distilled water.

(vii) After that it is dried in hot air.

3.2.2 Solution Chemistry:

Salt	Quantity
NiCl2	0.65M
NiSO4	0.30M
H3BO3	0.90M
CH3(CH)11OSO3Na (sodium dodecyl sulphate)	1.5gm/l

3.2.3 Preparation of electroplating solution for Ni-NiO electrode and electrodepostion.

Electrodeposition of Ni : Nickel is deposited on Aluminiun at 300mA /cm2 and 60 deg temperature through above galvanized dc supply .Then coated sample is cleaned with ethanol followed by acetone and dry at room temperature for some time.

Electrodeposition of Ni-NiO. : Nickel coated sample is deeped into 1M oxalic acid to get Ni-NiO. and solution is continuously revolve with help of magnetic bits to get uniform oxide surface.

Then coated sample is again clean with ethanol & acetone and dried to normal temperature over the night.

Fig 3.1 Electrodepostion Setup

3.3 Electrochemical Characterization of the developed electrocatalytic electrode materials:

In order to develop electrocatalytic electrode Ni-NiO & Ni-NiO-nano carbon coated electrodes were examined in different electrolytes system by studying cyclic voltammetry(CV), Chronoamperometry(CA), Potentiodynamic polarization(Pd) and Electrochemical Impedance Spectroscopy(EIS).

CV,CA and Pd experiments were performed in AMETEX VersaSTAT 3:Model-500

Picture is shown in figure 3.2

Fig 3.3AMETEX VersaSTAT 3: Model-500

Electrochemical impedance spectroscopy (EIS) experiments were performed in GAMRY Instruments which shows in figure…………

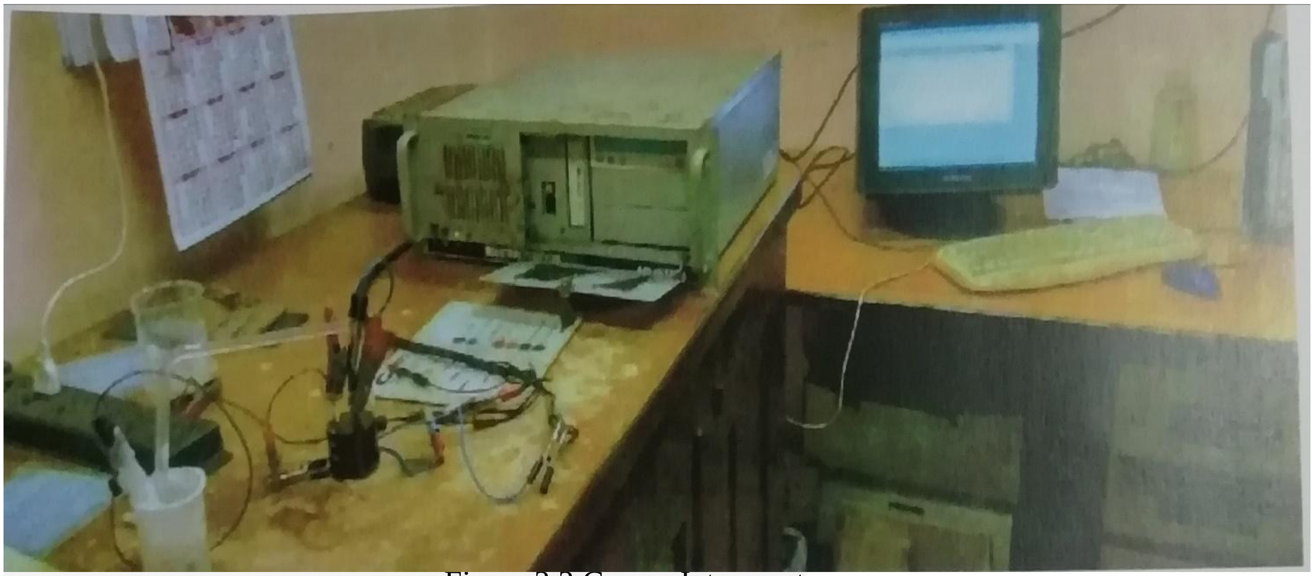


Figure 3.3 Gamry Intrument

3.3.1 Cyclic Voltammetry (CV):

Cyclic Voltammetry of the Al and Al-Ni coated foil was performed in a computer controlled electrochemical system machine, DY 2300 Potentiostat, with a three-electrode system to find out Imax (current amplitude). Here, the graphite rod was taken as counter electrode and saturated calomel electrode as reference electrode and test sample as working electrode. Potential was scanned -1V to 1V with scan rate 0.05 mV/second to find out Imax (current amplitude).

3.3.2 Chronoamperometry (CA):

The Chronoamperometry (CA) was tested in the same machine with different software. Experiment was carried out at different fixed potentials selected of -0.5V and - 1.0V. The current I was monitored as a function of time t to find out how long the steady state current is delivered from the cell. In the experiment time was taken up to 1000 sec.

3.3.3 Electrochemical Impedance Spectroscopy (EIS):

In EIS study, the experimental arrangement was same as that of polarization studies. The electrochemical cell was connected to an impedance analyzer(EIS300 controlled by Echem analyst software) for electrochemical impedance spectroscopy. The electrochemical impedance spectra were obtained at frequencies between 100 kHz and 0.1 Hz. The following results and information were obtained from the EIS experiments. Polarization resistance (Rp), electrolyte resistance (R.), double layer capacitance (Cdl), capacitive load or constant phase element (CPE (Y), and which is defined from the capacitive impedance equation Z=1/C(jw)-α

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE). The exponent α is 1 for ideal capacitance. For a constant phase element, the exponent, is less than one.

3.4 Physical Characterization of Materials:

Developed electro catalytic materials are physically characterized by XRD and SEM.

3.4.1 X-Ray Diffraction (XRD):

The crystalline structure and crystalline phase of the electrodes are characterized by XRD. The test was done using Rigaku Ultima III X-ray diffraction for recording the diffraction traces of the samples with monochromatic Cu Ka radiation at room temperature, at a scan rate of 2°/min. The crystallographic planes of X-ray diffraction were obtained from the inbuilt software of the X-Ray machine.

Fig…..XRD machine,model Rigaku Ultima III

3.4.2 Scanning Electron (SEM):

Microscope

The surface morphology and particle distribution of the electrodeposited composite coating were performed by using SEM.

CHAPTER 4

RESULT AND DISCUSSION

4. RESULT AND DISCUSSION

Ni and NiO-nano C energetic material synthesis by variation of electrode deposition parameters (such as) electrolyte chemistry, temperature, current density was characterised electrochemically by performing cyclic voltammetry, chronoamperometry, potentiodynamic polarization as well as electrochemical impedance spectroscopy to find out the best perform electrode on electro oxidation of ethanol fuel over the electrode surface. The following paragraph elaborately describes the experimental curve and computed data to compare electrochemically energy giving properties of the different electrodes produce by different treatments.

The morphology of electrode surface was examined by scanning electron microscope and the constituent of the phases were found out by XRD analysis. The details of the experiment procedure are discussed in the section 3.

4.1 CYCLIC VOLTAMMETRY

Cyclic voltammetry is performed to know how much maximum current enhance energy can be obtained on electro oxidation of ethanol fuel on the anode surface. Figure 4.1 show the CV of Ni-NiO electrode produce at different electrodeposition current density. It is interesting to find out that the maximum current value i.e., the maximum current density achieve increases with increase in deposition current density till it achieves at an optimum value of deposition current density(300mA/cm^2). There after increase in current density decrease the maximum current. The electrochemically energy contain is given by the area under the CV curve.

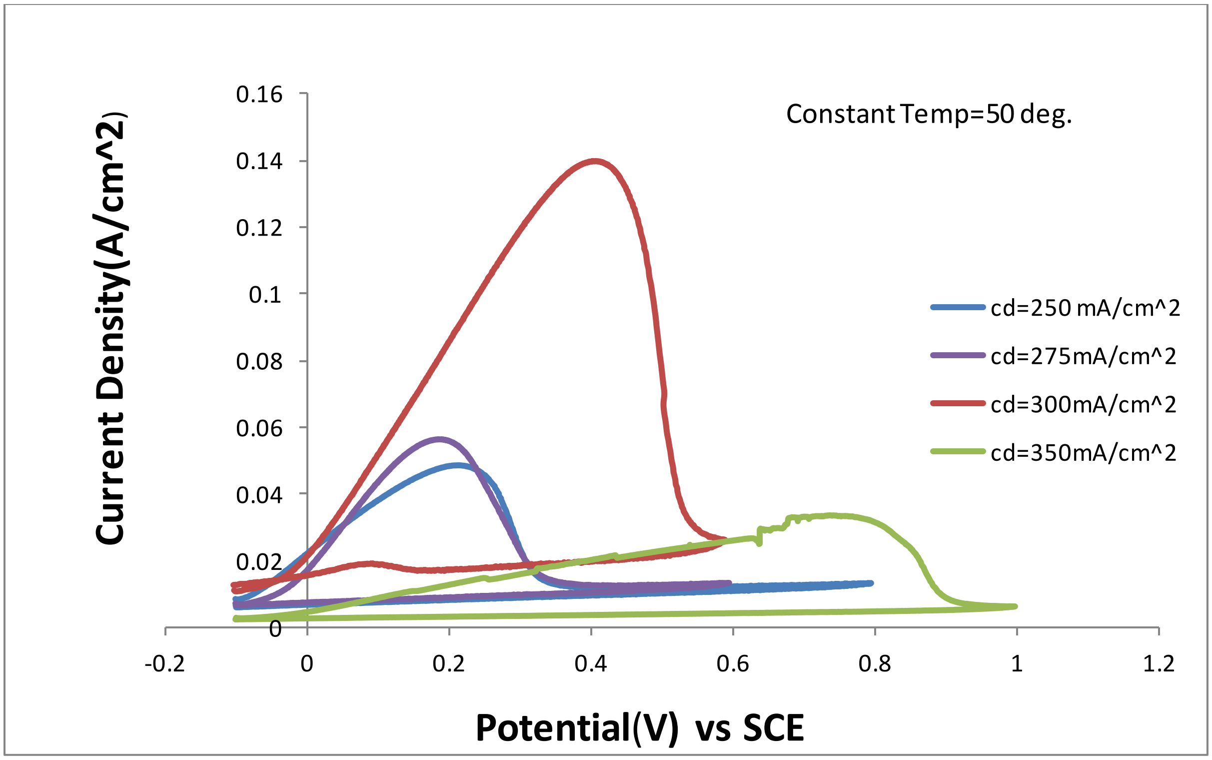


Figure 4.1 show the CV of Ni-NiO electrode produce at different electro deposition current density.

Increases in current density of electrodeposition supplies more electrons charge density on the cathode surface. Now the cation Ni^{++}accumulated near the electrode surface will be immediately discharge and deposited on the electrode surface by accepting electron from it. The deposition material would be formed by nucleation and growth. The deposition potential is given by the following equation for

$$\mathbf{M^{+} + \ ne^{-}} \qquad \mathbf{M} \longrightarrow$$

$E_d = E + RT/nF \log[M^+] + n_{act} + n_{con} + IR$

So, the minimum potential to deposit a metal atom is dependent on overvoltage and solution resistance besides the electrode potential. If the temperature is more than the n_{conc}will decrease as diffusion boundary layer thickness decreases and mobility of the ion increases due to convection.

After all the metal ions at the electrode boundary have been deposited the electrons on the electrodes surface need to wait for new ions to diffuse from the bulk of the solution towards the electrode ssurface. With higher current of deposition to much electrons are accumulated in the electrodes making it highly negatively charged, it will capture charge impurities from the solution or impure gases from the environment such as ammonia,surphur-tri-oxide, carbon dioxide etc to reduce its charge and thereby the electrodes are contaminated by small amount of nonconductive impurities entrapped. This decreases the maximum current a little bit. So that’s why it is needed to find out the optimum current density produced best performed electrodes.

4.1.1 Effect of fuel temperature:

Figure 4.2 depicts that CV of the best perform electrode material with variation of fuel temperature. It is seen that both the maximum current density and energy contain increases with increase in fuel temperature.

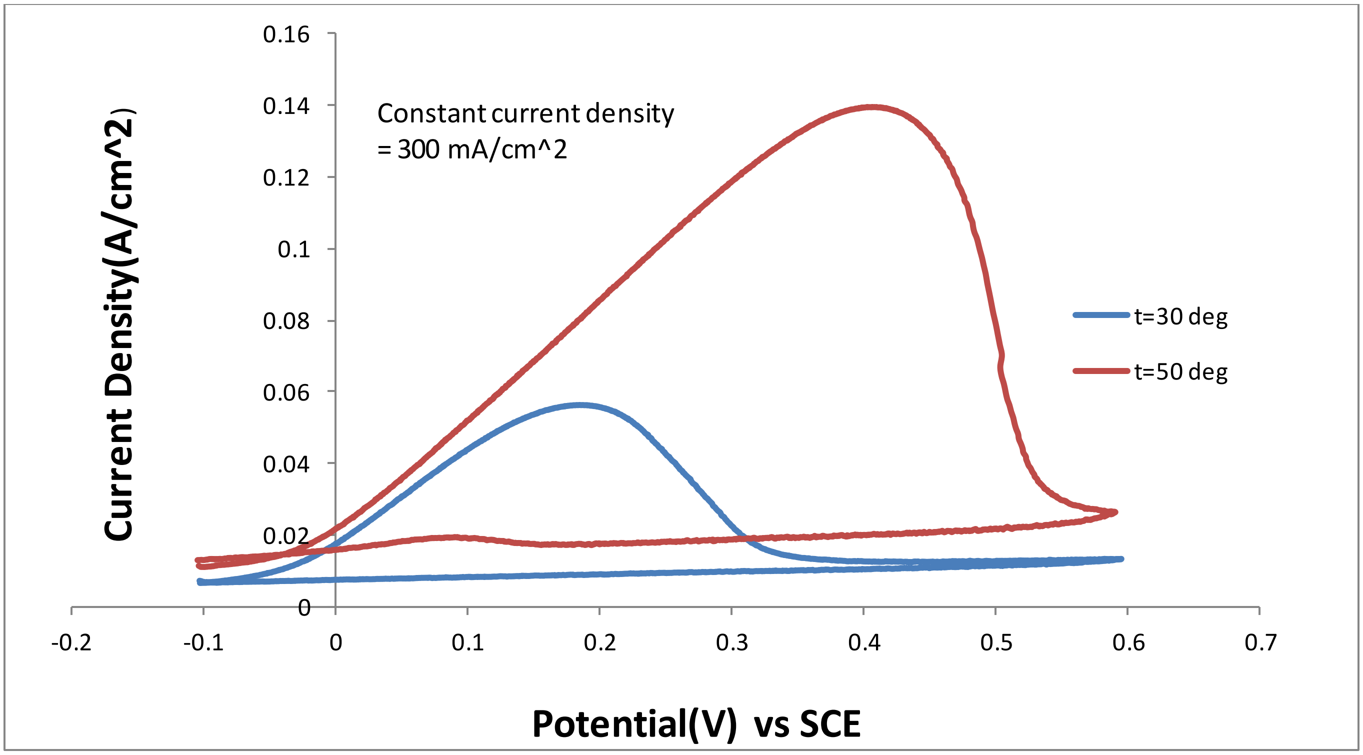


Figure 4.2 CV of the best perform electrode material with variation of fuel temperature.

4.1.2 Effect of nanocarbon on Ni-NiOelectrode.

The electrode has been further modified by depositing nanocarbon over Ni-NiO electrode surface.

Fig 4.3 shows the cv with and without nanocarbon addition. it clearly indicates that addition of nanocarbon makes it a Ni-NiO nanocarbon composite has enormously increased the energy delivered by the electrode on electro oxidation of fuel over the electrode surface.

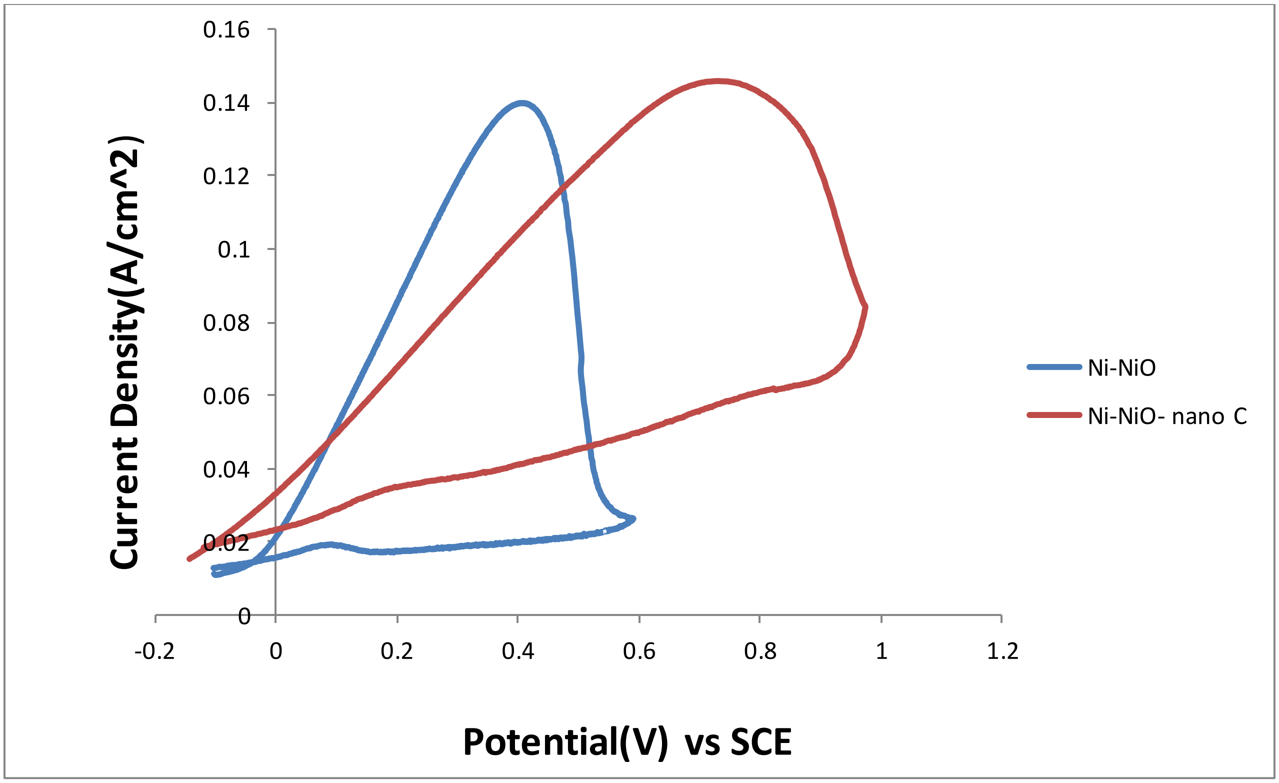


Fig 4.3 shows the CV with and without nanocarbon addition.

4.2 Chronoamperometry

Having obtained high energetic electrode with very good maximum current density and energy content. it is interesting to find out how the current decays with time by performing Chronoamperometry test.

Fig 4.4 shows that the chronoamperometry of electrode produce at different current density. it is seen that the current density increase or decrease initially with about 30-40 seconds than the current becomes steady. It is interesting to see that the best performing electrode having a steady state current density of above 6 A per 100cm2 electrode surface area and the single figure with addition of nanocarbon as produce of as much as 100 A current per 100cm2 electrode surface area which is very good performance.

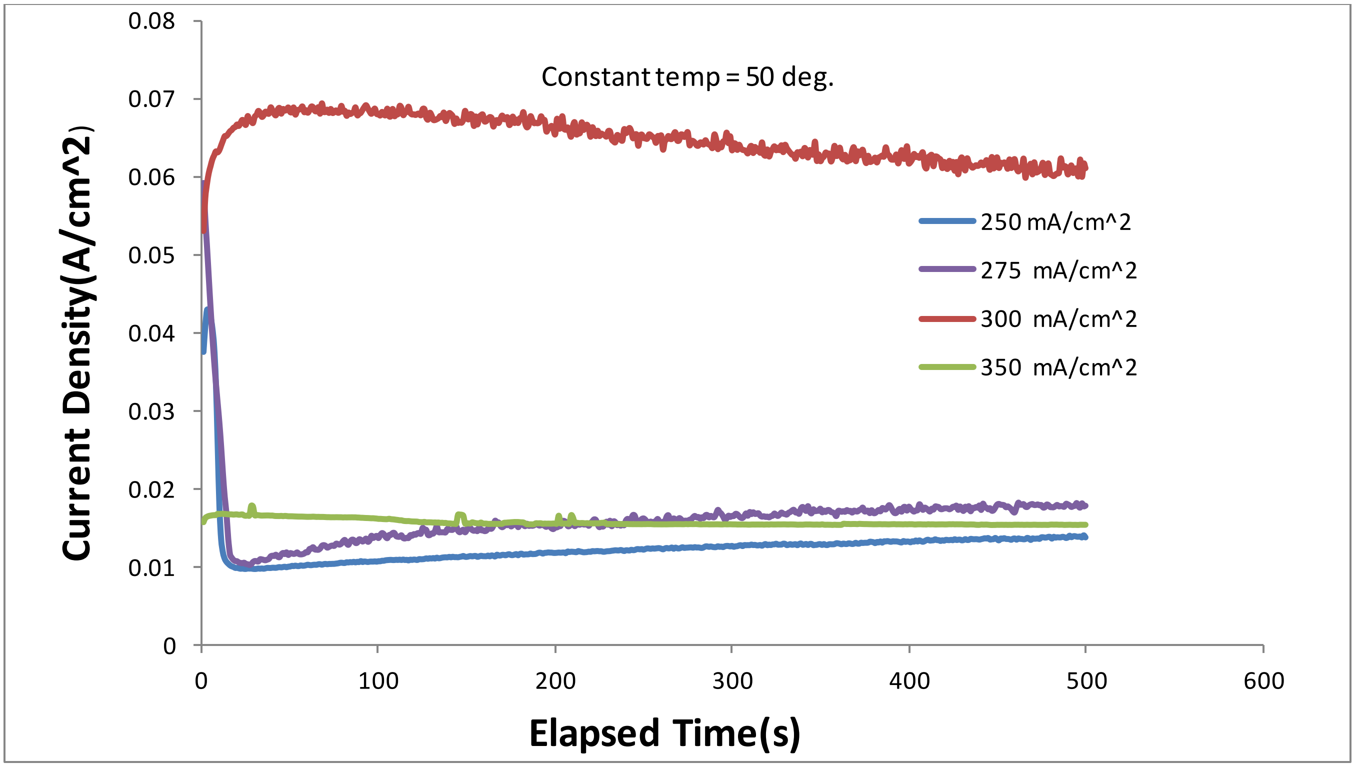


Fig 4.4 shows that the chronoamperometry of electrode produce at different current density.

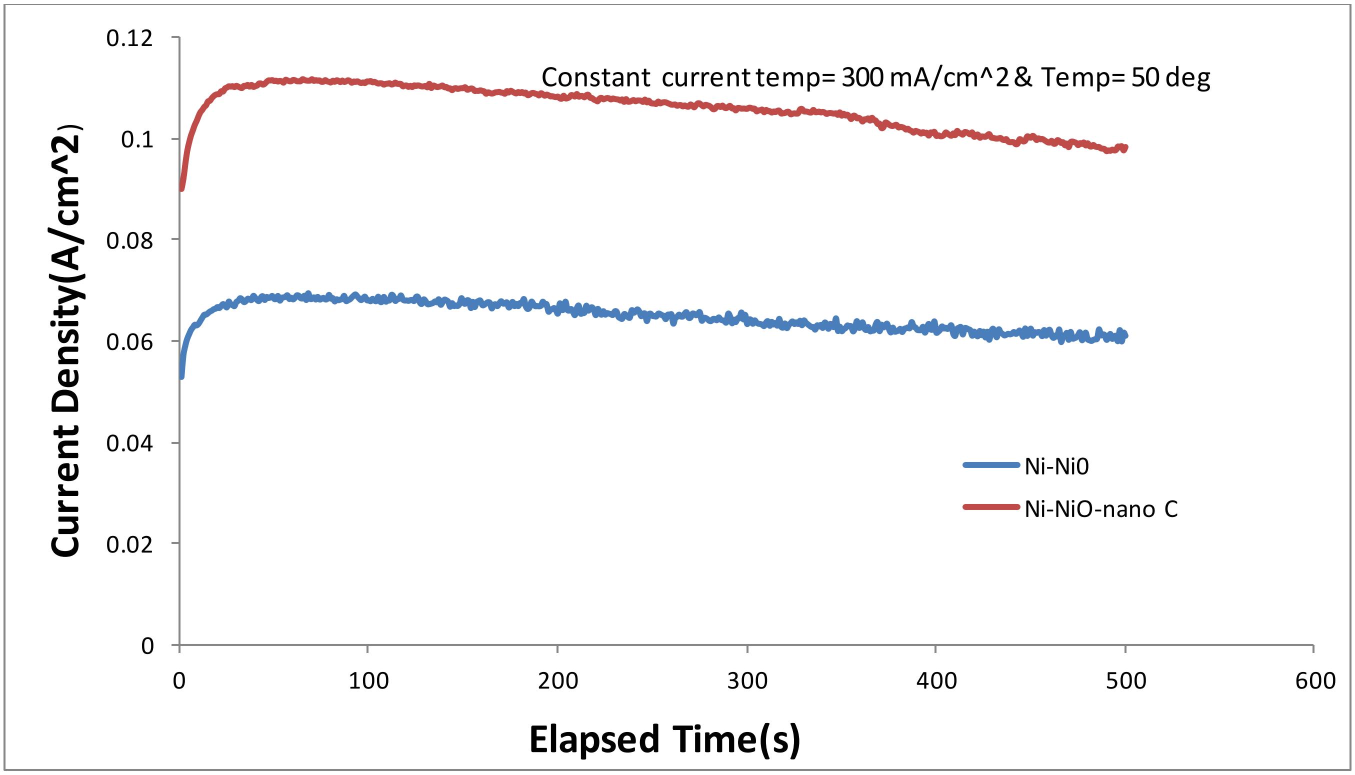


Fig 4.5 shows the CA with and without nanocarbon addition.

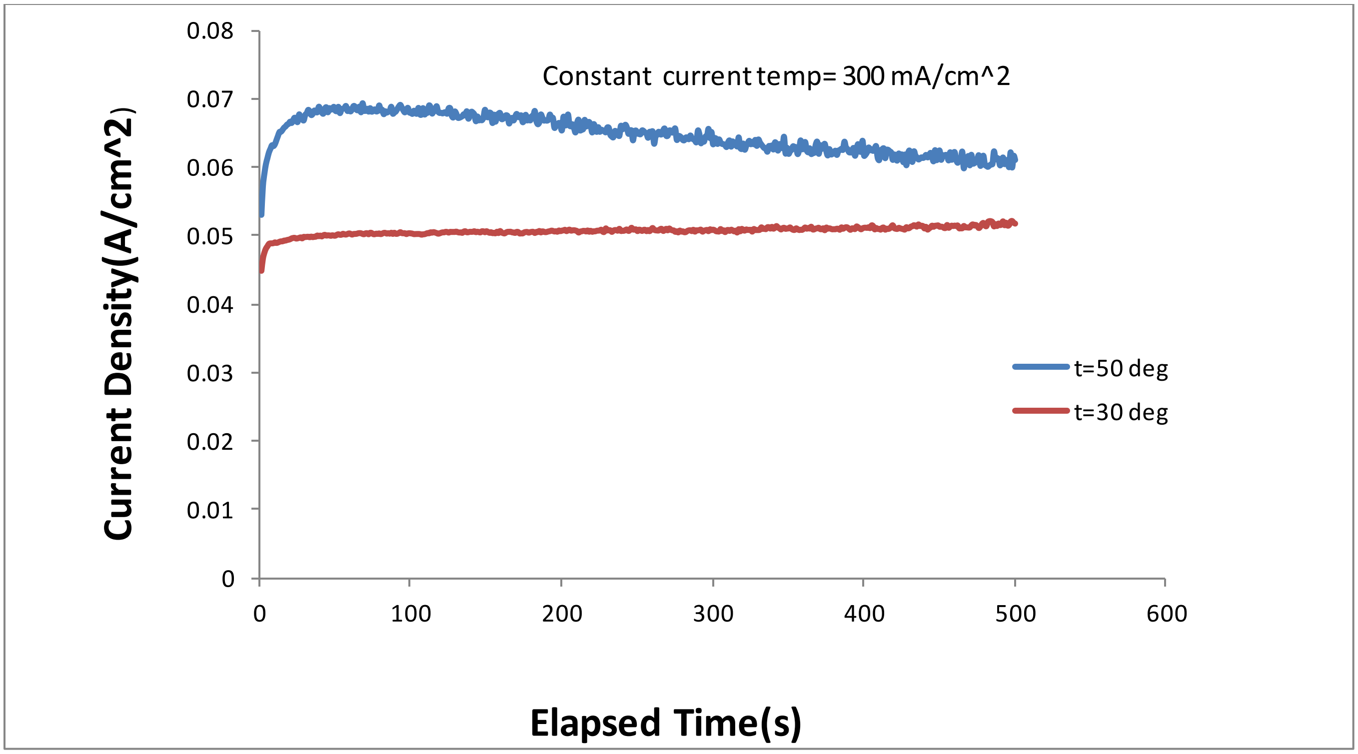


fig 4.6 Effect of temperature variation of fuel of chronoamperometry supply .

4.3 Potentiodynamic Polarization:

Having obtain good electrocatalytic material of Ni-NiO in CV and CA studies the potentiodynamic polarization(Pd) studies are done only best electrodeposited material as found by CV and CA investigation.

Figure 4.7 shows Pd studies of Ni-NiO electrodeposited at various current density . The reversible maximum cell current density for all these materials are found to be over 50mA/Cm^2 which is very satisfactory.

A cell build with an electrode surface area of 20cm2 will produce about 1A current and that can drive a motor.So, the result are satisfactory.

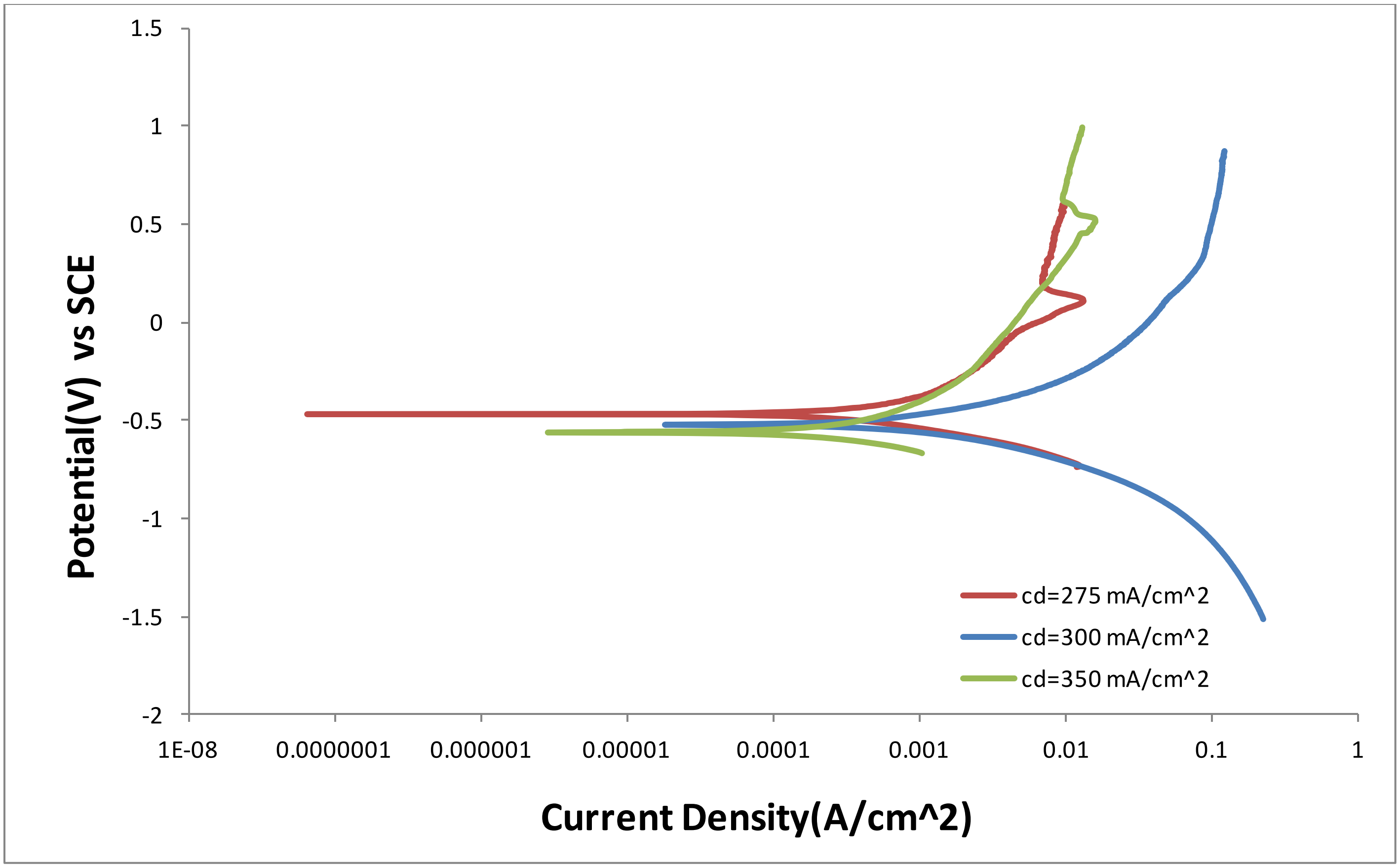


Figure 4.7 show the Pd of Ni-NiO electrode produce at different electro deposition current density.

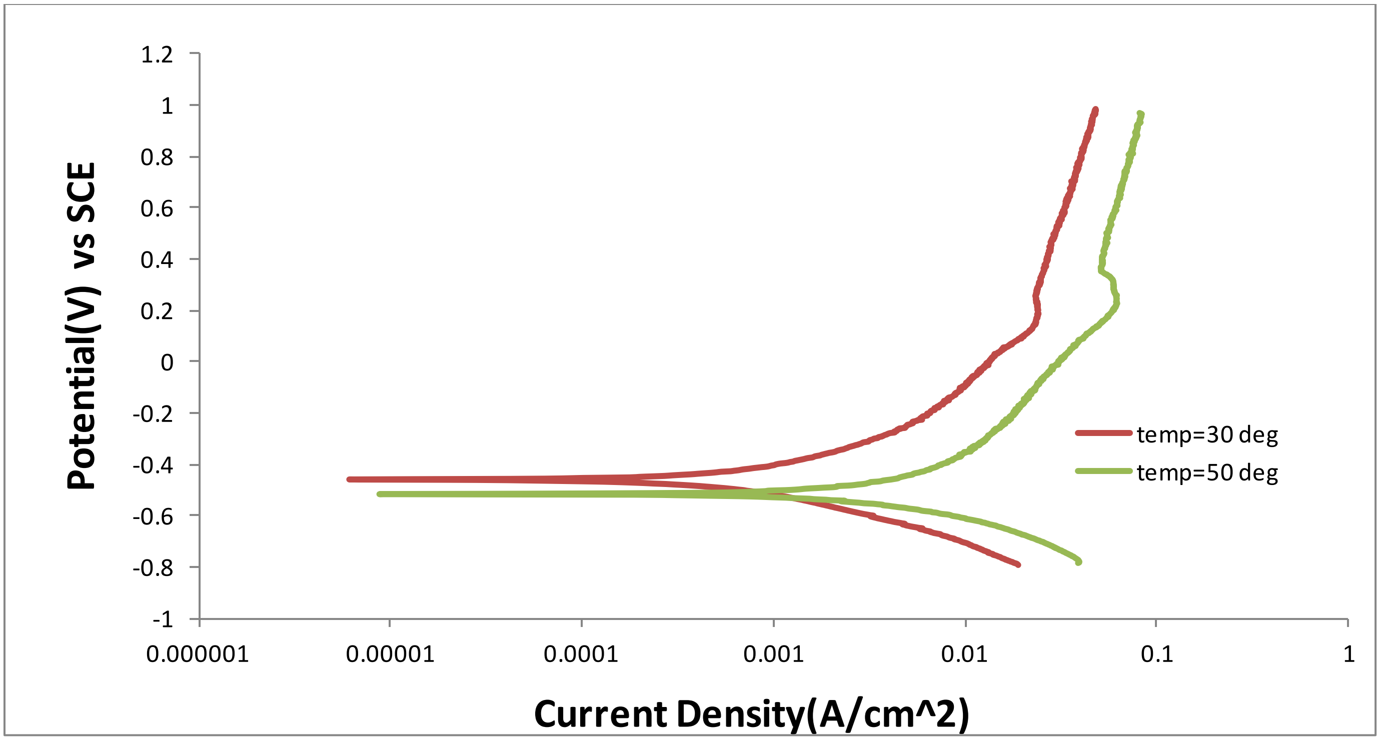


Figure 4.8 Pd of Ni-NiO electrode material with variation of fuel temperature.

4.4 Electrochemical impedance spectroscopy

The electrochemical phenomena occurring at the metal-electrolyte interface can be represented by R-L-C circuit and is studied by EIS for better understanding of the fundamental aspects of oxidation of the fuel on the electrolytic substrate. In general, the interface consists of layer of (+ve) charge and a layer of (-ve) charge which is called electrical double layer, which produce a capacitance or pseudo-capacitance. In addition, there are resistance load for polarization resistance (Rp), solution resistance (Rs). There may also be induction or morecapacitance due to coating. The phenomenon can be interpreted by Nyquist and Bode plot, which are depicted and discussed in the following section for Ni and Ni based nanoC coated electrode.

EIS studies of Ni and Ni based nanoC are shown in figure 4.9 (Nyquist plot) and figure 4.10 and Bode plot. The Nyquist shows a branch of semicircle with decreasing diameter. The electro coating carries nanoC shows the minimum polarization resistance and hence high electrocatalytic material. The Bode plot Shows the similar trend, impedance more when the material is Ni-NiO. The phase angle vs frequency plot indicates one capacitance for each of the curve. It follows a Randle circuit and the capacitance is not a pure one but a pseudo capacitance the phase angle or lags-35 degree to -65 degree which indicates pseudo capacitance. The computed EIS parameters are shown in Table Number 4.4

Electrolytes	Anode	Cathode	Rp	Ru	type
1M Ethanol +1M KOH	Ni-NiO (electrodeposition at 60 deg & 300mA/cm2 in 1M axalic acid	Porous graphite rod	9.0	6.0	Randle model
1M Ethanol + 1M KOH	Ni-NiO-nanoC	Porous graphite rod	5.0	9.0	Randle model

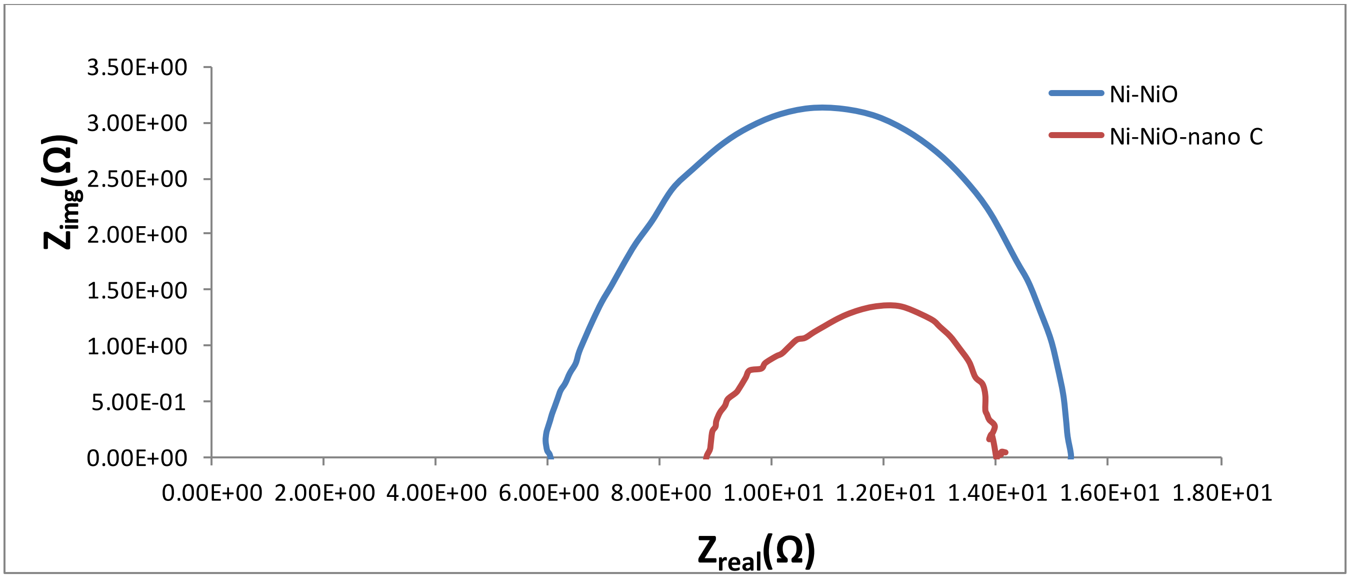


Fig 4.9 Nyquist plot with and without addition of nano carbon.

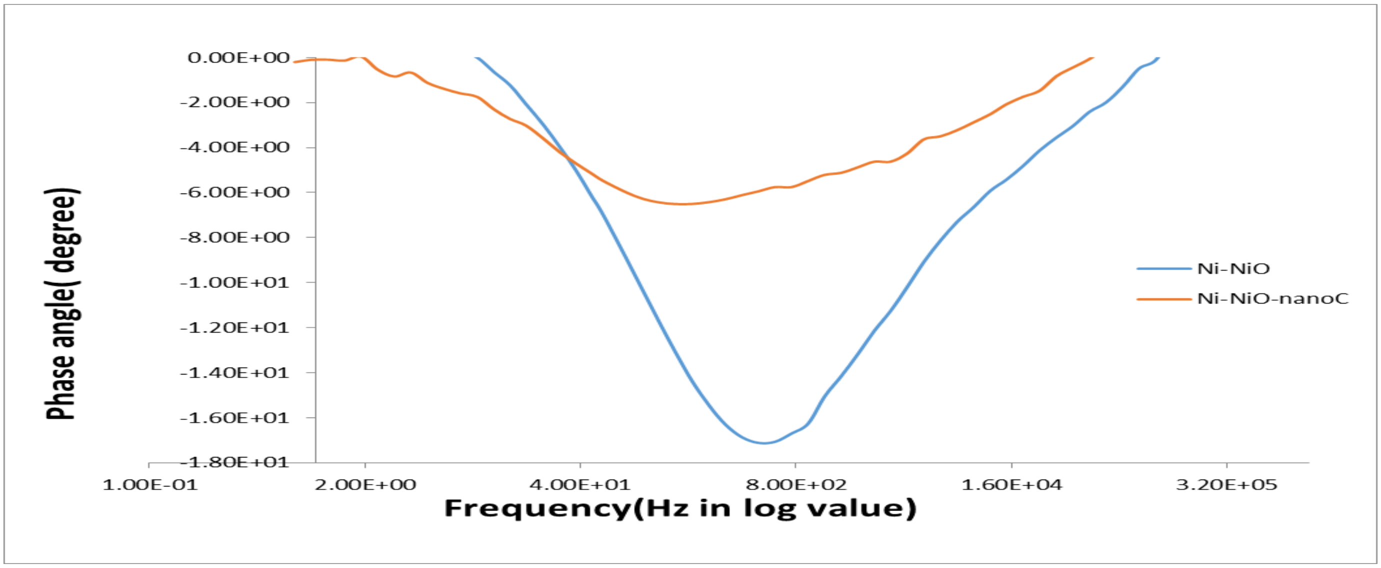


Fig 4.10 pangle vs frequency curve with and without addition of nano carbon.

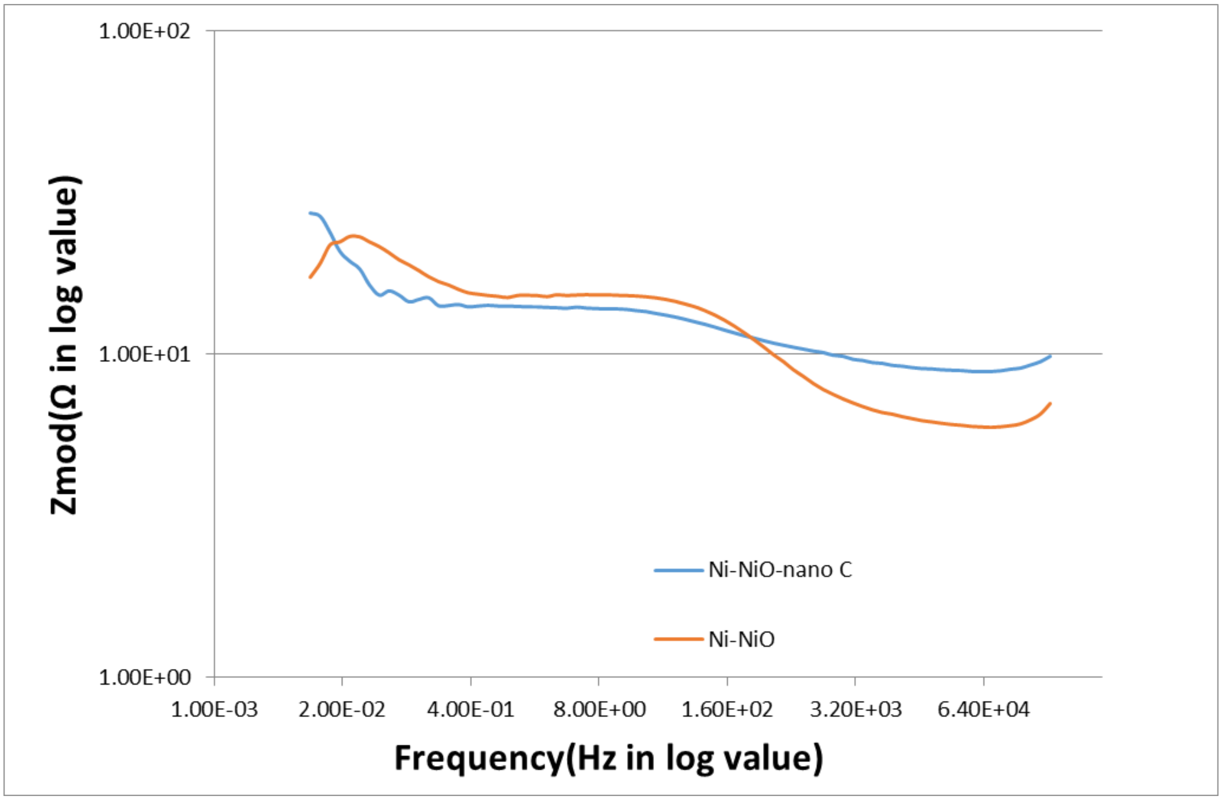


Fig 4.11 Zmod v/s Frequency curve with and without addition of nano carbon.

4.5 PHYSICAL CHARACTERIZATION

4.5.1 XRD

The electrodeposition electrocatalytic materials are studies by XRD to know the constituent of the electro coating.

Figure 4.12 shows the XRD graph of Ni-NiO electrocatalytic material. It is seen that instead of NiO non-stoichiometric nickel hydroxide has formed along with pure Ni, the component being a defect semiconductor oxide has got anion deficiency and excess cations which will produce positively charged electron holes. This helps faster charge discharge reaction at the interface of solid electro-liquid fuel producing high charge density. This explains high current delivered on electrooxidation of ethanol on Ni-NiO electrode surface.

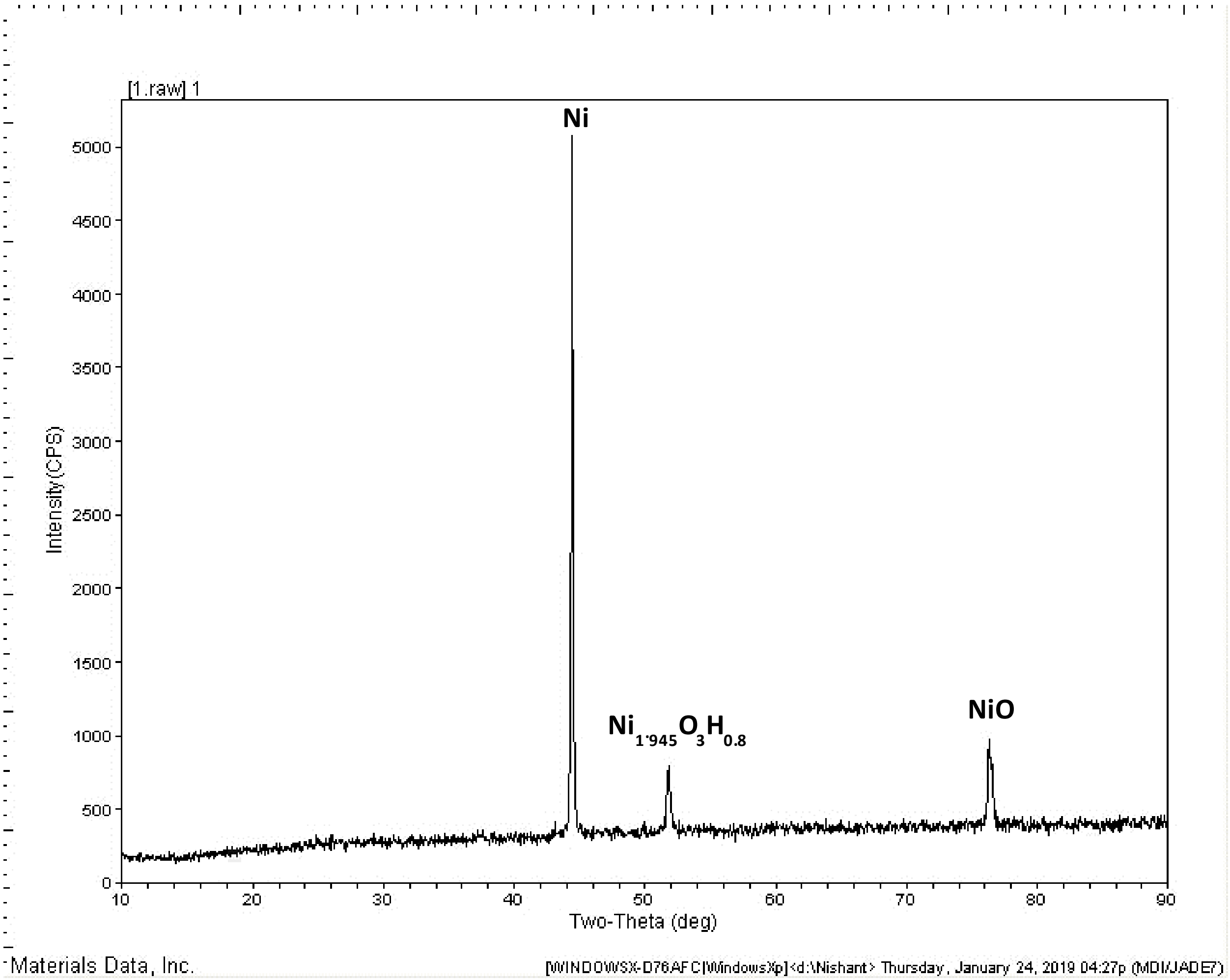


Fig 4.12 :XRD of Ni-NiO

Figure 4.13 shows the XRD graphs of Ni-NiO-nanoC Eelectrocatalytic material. It clearly reveals presence of small amount of nano carbon with Ni. This indicates that the electrocatalytic material developed in a composite of Ni and Ni based nano C which produce very good electrocatalytic effect for electrooxidation of ethanol ,giving high current.

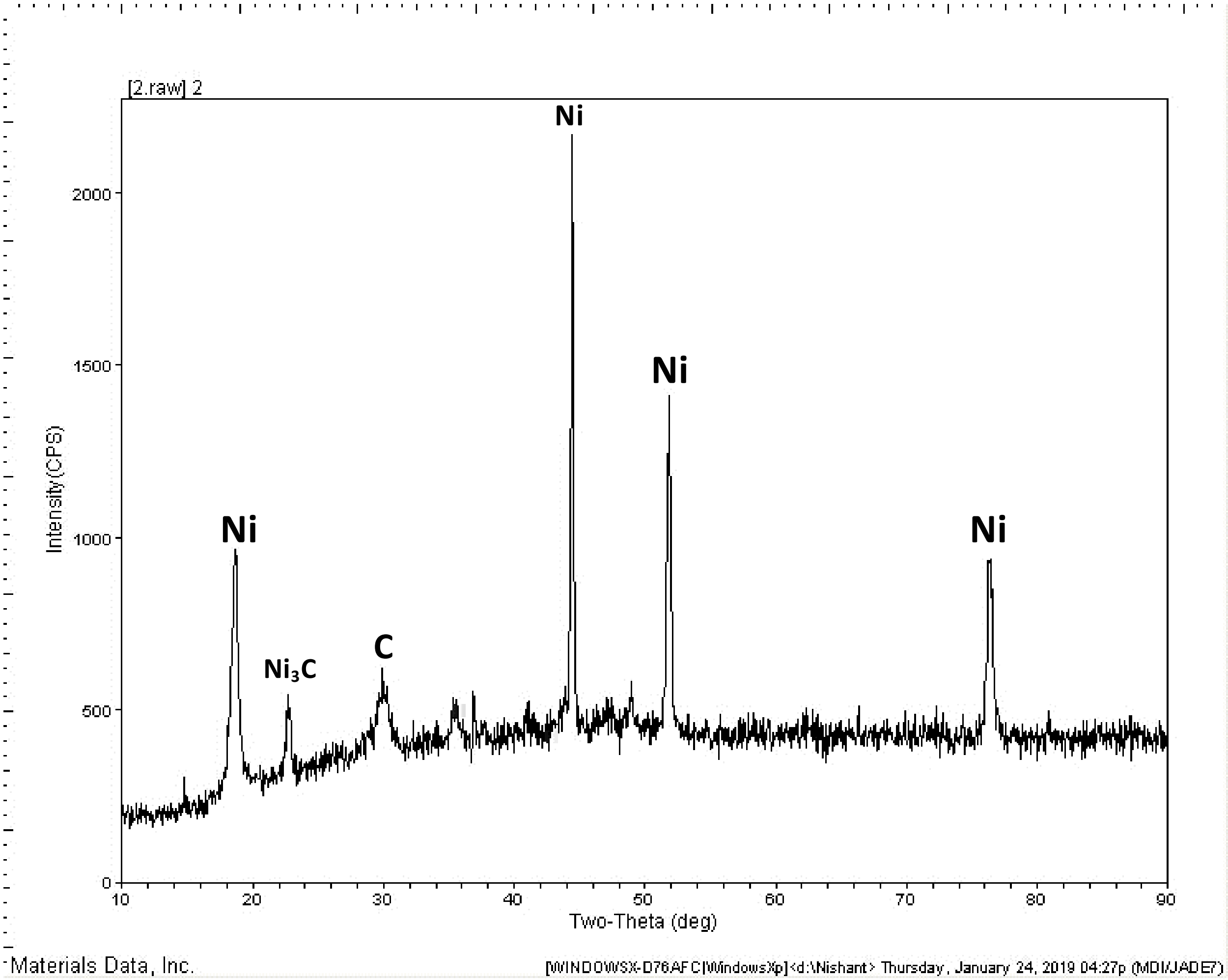


Figure 4.13 XRD of Ni based nano carbon material.

4.5.2 SEM

Having obtained the constituent of electrocatalytic materials by XRD studies ,it will be interesting to know the morphology of coated electrodes under scanning electron microscope .fig 4.14 shows the scanning image of Ni-NiO electrocatalytic material.It is seen the precipitated distribution throughout the surface in spherical and subspherical globular forms with channels and inter channels in between.The nano channel and inter channels with micro to nano grains make effective surface area for change discharge reaction by many times more than the geometrical electrode surface .This make huge charge density and the current delivers is very high .So, this morphology of the scanning image support the high current obtained in CV , CA ,Pd studies.

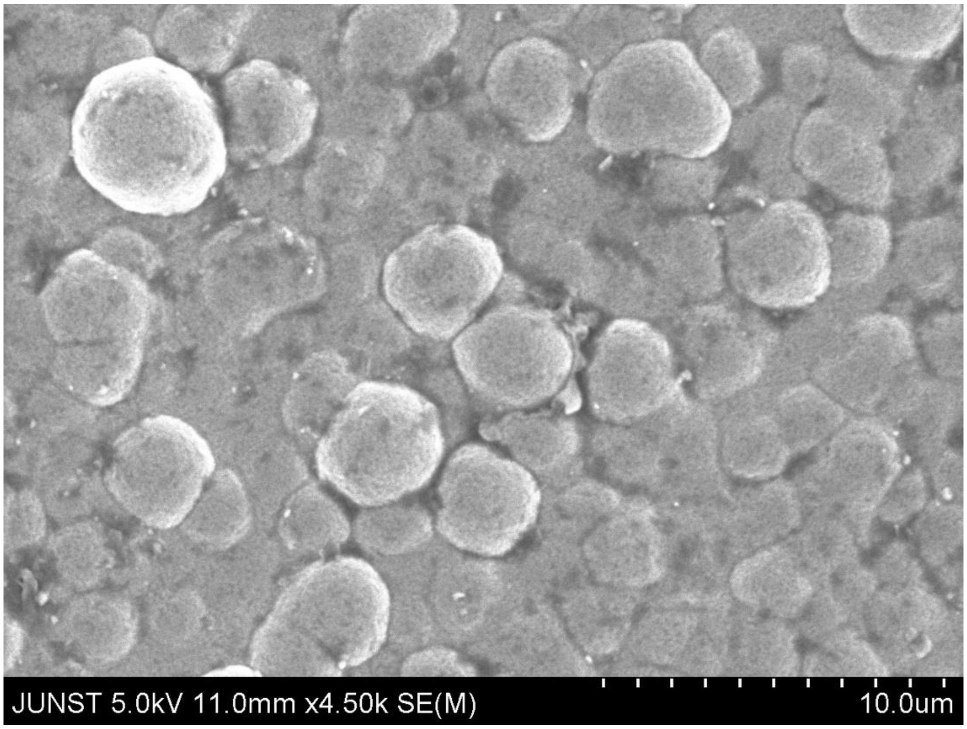


Fig 4.14 SEM micrographs of the coated sample of Ni-NiO

CHAPTER 5

CONCLUSIONS

CONCLUSION

From the forgoing results and discussions following statements can be concluded-

1. Addition of Nano Carbon to NiO enhances the electrocatalytic activity for oxidation of ethanol fuel. It increases cell current and energy

2. The EIS studies and its results support the high current density obtained for those electrocatalytic materials in CV,CA,PD studies and have confirmed the addition of nano carbon is beneficial.
3. The XRD studies display the presence of Ni,NiO and nickel based nano carboon phases which are responsible for high current density for electro oxidation.

4. The morphpological image analysis of the coated surface is observed under SEM show ………………………….. The image supports much higher 3D electrocatalytic surface area available for electro-chemical oxidation of fuel which produces high current as obtained in electro-chemical characterisation.

5. The present investigation opens up a new way and technology of producing energy at a economically viable rate, compared to conventional electrical energy production, using ethanol solution

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